EVALUATION OF EFFECTIVENESS OF PHOSPHATE AND ZINC AS SCALE INHIBITOR IN DELAYING PRECIPITATION OF $CaCO_3$

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December, 2020

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A Thesis submitted by

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In partial fulfillment of the requirements for the Degree of

MASTER OF SCIENCE IN CIVIL ENGINEERING (ENVIRONMENTAL)

DEPARTMENT OF CIVIL ENGINEERING BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY DHAKA, BANGLADESH

December, 2020

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Signature of the Candidate

Ishrat Rashid

Dedicated to my parents

Dr. Md. Abdur Rashid
and
Khadija Akhter

ACKNOWLEDGEMENT

First of all, the Author would like to express her deepest gratitude to the gracious Almighty Allah for His unlimited kindness and blessings to fulfill the thesis work successfully.

The Author wishes to express her heartiest gratitude and sincere thanks to her supervisor Dr. Muhammad Ashraf Ali, Professor, Department of Civil Engineering, BUET for his proper guidance, invaluable suggestions and continuous supervision at all stages of this research work. The Author is indebted to him for his affectionate encouragement and endless contribution to new ideas and helpful co-operation throughout the thesis work. The Author also appreciates his sincere effort, which came to great help to write this thesis.

The Author would also like to gratefully acknowledge the support and assistance provided by Dr. Ehosan Habib, Mr. Rafiqul Islam Mithu, Mr. Md. Mahbubur Rahman and Mr. Muhammad Enamul Haque of Environmental Engineering Laboratory, Department of Civil Engineering, BUET. The Author would also like to thank Ms. Tahsina Alam and Mr. Tasnim Ahmed for their assistance. The Author would like to render her thanks also to the teachers of the Department of Civil Engineering, BUET for their sincere help. The Author would like to express a very special indebtedness to her parents whose encouragement and support were a continuous source of inspiration for this work. Finally, the Author would like to thank all who helped her in making a successful and productive completion of the thesis.

BUET, Bangladesh Ishrat Rashid

December, 2020

ABSTRACT

Precipitation of $CaCO_3$ has long been a concern in water treatment and distribution systems; however, this problem has been identified only recently in some areas (e.g., in Meherpur) of Bangladesh. The potential methods for control of $CaCO_3$ precipitation in the context of Bangladesh include lowering of pH, removal of Ca, and delaying/preventing precipitation using scale inhibitor. Scale inhibitors can prevent or delay precipitation by adsorbing onto the active crystal growth sites of calcite (a polymorph of $CaCO_3$), thereby delaying or reducing precipitation.

This study presents an assessment of the potential effectiveness of phosphate and zinc as scale inhibitors in reducing the precipitation of $CaCO_3$ in water. This work involved laboratory batch experiments in electrolyte (NaCl) solution in deionized water (in order to eliminate possible effects of constituents that could interfere with $CaCO_3$ precipitation, e.g., Mg^{2+}, silica) containing calcium chloride and sodium bicarbonate. Phosphate was added to the solution as potassium dihydrogen phosphate solution, and zinc was added as zinc chloride solution. Subsequently, similar batch experiments were carried out with natural groundwater. In addition, behavior of the experimental systems under "equilibrium" condition was simulated using MINEQL+ chemical equilibrium model. Effect of PO_4^{3-} and Zn^{2+} on precipitation of $CaCO_3$ was evaluated as a function of inhibitor concentration (varying from zero to 5 mg/l), mixing time (varying from 30 minutes to 5 hours), and the degree of super-saturation.

In electrolyte (NaCl) solution in deionized water, for a particular degree of super-saturation and mixing time, precipitation of $CaCO_3$ decreased as inhibitor (either phosphate or zinc) concentration increased. The effect of phosphate or zinc in inhibiting precipitation of $CaCO_3$ has been found to be more pronounced at lower concentrations of the inhibitors. One interesting observation from these experiments was that the inhibition effect of Zn increased with time, while that of phosphate decreased with time. But this trend becomes less pronounced at higher inhibitor concentrations. However, in experiments with natural groundwater, neither phosphate nor zinc could reduce the precipitation of $CaCO_3(s)$; in fact, precipitation slightly increased with addition of phosphate and zinc. From MINEQL+

analysis, it appears that this could be due to possible enhanced precipitation of $CaCO_3(s)$ [and also dolomite, $CaMg(CO_3)_2(s)$] in the presence of silica (which is present in high concentration in natural groundwater), possible precipitation of Ca-PO_4 solids, and possible formation of $ZnCO_3(s)$ (that would limit availability of Zn^{2+}). Therefore, phosphate or zinc cannot be recommended as inhibitors (of calcium carbonates) in natural groundwater; more studies are needed focusing on the effect of silica on precipitation of calcium carbonate and precipitation of other solids in complex groundwater systems.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
ACC	Amorphous Calcium Carbonate
AWWA	American Water Works Association
BOD	Biochemical Oxygen Demand
CNT	Classical Nucleation Theory
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DoE	Department of Environment
EC	Electrical Conductivity
ECR	Environmental Conservation Rule
K_{sp}	Solubility Product Constant
MINEQL+	Chemical Equilibrium Modeling System
NOM	Natural Organic Matter
RO	Reverse Osmosis
TDS	Total Dissolved Solids
PNC	Pre-nucleation Cluster

CHAPTER 1

INTRODUCTION

1.1 Background

Scaling in natural hard water is a major concern in different fields of industrial processes and domestic installations. Undesirable scale deposits often cause numerous technical and economic problems such as total or partial obstruction of pipes leading to a decrease in flow rate; reduced heat transfer as calcium carbonate precipitate is 15 to 30 times less conductive than steel; seizure of valves and clogging of filters etc. This scale formation is the result of changes in the ionic composition, pH, pressure and temperature of the brine [1-2]. The scales consist primarily of carbonates, sulfates, hydroxides, phosphates, and silicates of alkaline earth metals, particularly calcium and magnesium. The problem of scale formation is intensified at higher temperatures because of the peculiar inverse temperature - solubility characteristics of these minerals in water [3].

The prediction, monitoring, and consequences of $CaCO_3$ formation have long been a key issue in potable water treatment. An early concern was that waters highly under saturated with $CaCO_3$ would be corrosive to metallic and concrete pipe infrastructure [4], and for waters highly supersaturated with $CaCO_3$, issues related to scaling (i.e., pipe clogging, head loss, higher heating costs) are the primary concerns [5]. In the 80+ years since the landmark studies examining these issues were published, many changes have occurred that can profoundly alter the likelihood of $CaCO_3$ scaling in potable water systems including chemical corrosion control, changing water heater set-point temperatures, autogenous repair, global warming, biofilm growth, and erosion corrosion [6].

The precipitation of $CaCO_3$ (in water containing high concentration of Calcium and Carbonate) has long been a concern in water treatment and distribution systems; however, this problem has been identified only recently in Bangladesh [7]. Scaling is the most obvious manifestation of $CaCO_3$ precipitation in water distribution systems, resulting in flow restrictions in the system by clogging of pipes, plumbing devices and creating head loss [8].

Globally, the scaling issue is reemerging, particularly due to climate change and temperature increases in hot water systems (since higher temperature promotes $CaCO_3$ precipitation). The common methods available for control of $CaCO_3$ precipitation include: (a) lowering pH of water; (b) removal of dissolved Ca; (c) delaying or preventing $CaCO_3$ precipitation using scale inhibitor; (d) decreasing water temperature; (e) controlling $CaCO_3$ morphology; and (f) control the use of surface materials (e.g., pipes) [6].

Among these, the first three are potential methods in the context of Bangladesh. The last three methods do not seem to be practical in the context of Bangladesh. Decreasing water temperature is primarily applicable in the context of water heaters, controlling calcium carbonate morphology is technically challenging, while changing surface materials (e.g. pipes, fixtures) is difficult and this is unlikely to bring about significant benefits. In Bangladesh, groundwater often contains high concentration of Fe (and in some places As), and lowering of pH of water adversely affects removal of iron (and also As) by conventional treatment. Conventional treatment typically involves aeration to facilitate precipitation of iron by introducing oxygen in water and raise pH by driving away excess carbon-di-oxide from water. Removal of arsenic takes place by co-precipitation and adsorption onto iron hydroxide flocs, which are removed from water using granular filter media. Removal of Ca from water by raising pH has a number of major operational difficulties, including controlling actual location of precipitation. Without precise control, precipitation could take place over filter media (in a treatment plant), or even in the transmission/ distribution system. Removal of Ca by other means (e.g., ion exchange resins) at municipal /city scale often becomes prohibitively expensive [7]. Different types of scale inhibitor (e.g., Mg^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, phosphates) have been used for delaying precipitation of $CaCO_3$ [6, 9-13]; the scale inhibitors work by preventing either precipitation and/or by adsorption onto calcite active crystal growth sites, thus preventing/delaying crystal formation [14-15]. It can also affect the nucleation and crystallization rates of $CaCO_3$ and induce morphological changes of the crystal shape [1-2].

As noted earlier, $CaCO_3$ scaling is a newly identified problem in Bangladesh, and inhibitors have never been used in any water treatment systems in Bangladesh. Among the common inhibitors, Mg^{2+} and SiO_2 are often present at relatively high concentration in groundwater of Bangladesh; precipitation of $CaCO_3$ in their presence (as observed in Meherpur Paurashava) suggest their limited effects on $CaCO_3$ precipitation. Some inhibitors (e.g., Ni^{2+} and Cu^{2+}) cannot be used in water supply because of their low tolerance level in drinking water (Bangladesh drinking water standard for Ni^{2+} and Cu^{2+} are 0.1 and 1.0 mg/l, respectively). Therefore, phosphate and Zn^{2+} (with drinking water standards of 6.0 and 5.0 mg/l, respectively) appears to be potential inhibitors for use in water supply systems. There is however limited data on inhibition effect of orthophosphate and Zn^{+}. It is therefore important to assess the effects of these inhibitors on $CaCO_3$ precipitation in the context of Bangladesh. Results of such research works could lead to a possible solution to the scaling problem in Meherpur Paurashava and similar other areas of Bangladesh would be developed.

1.2 Objectives of the Research with specific aims and possible outcome

The overall objective of the research was to assess the effectiveness of phosphate and zinc as scale inhibitor in delaying precipitation $CaCO_3$ in water containing high concentrations of calcium and carbonate.

Specific objectives include:

(1) Evaluation of the precipitation of $CaCO_3$ in the presence of phosphate in NaCl electrolyte solution (in deionized water) under a range of experimental conditions, including time, pH, and degree of supersaturation.

(2) Evaluation of the precipitation of $CaCO_3$ in the presence of Zn^{2+} in NaCl electrolyte solution under a range of experimental conditions, including time, pH, and degree of supersaturation.

(3) Evaluation of precipitation of $CaCO_3$ in the presence of phosphate and Zn in natural groundwater, and assess possible application of phosphate and/or Zn^{2+} to prevent/reduce scaling in water treatment and distribution system.

1.3 Outline of Methodology

At first, effect of the phosphate and Zn inhibitors was evaluated in batch experiments. The batch experiments were carried out in 0.1 M NaCl solution (in deionized water) instead of groundwater, in order to eliminate possible effects of constituents that could interfere with $CaCO_3$ precipitation (e.g., Mg^{2+}, silica). In these experiments, concentrations of Ca and carbonate in water were varied to achieve the desired degree of supersaturation (Ω). Reagent grade $CaCl_2$ and $NaHCO_3$ were used to prepare stock solutions of Ca and carbonate/bicarbonate, which were used to achieve the required concentrations of Ca and carbonate in water and thus required Ω. Concentrations of H_2CO_3, HCO_3^- and CO_3^{2-} were determined based on the total concentration of inorganic carbon (C_T) or measured total Alkalinity added to the system (in the form of $NaHCO_3$ stock solution) and pH. In a series of volumetric flasks specific concentrations of Ca and carbonate solutions were taken. Then phosphate or Zn inhibitor was added at concentrations varying from zero to 5 mg/l. After the end of specific reaction time (varying from 30 minutes to five hours), about 50 ml water sample was collected from each beaker. Then they were filtered through 0.45 µm filter paper in order to filter out any precipitated $CaCO_3$. The supernatant was then analyzed for dissolved Ca concentration. Similar experiments were carried out with natural groundwater (collected from a deep tube well pump station of BUET), in order to evaluate the effect of phosphate and zinc inhibitor on precipitation of $CaCO_3$ in groundwater containing diverse chemical constituents. In addition, MINEQL+ simulations were carried out to understand the behavior of the experimental systems under "equilibrium" conditions. Based on the experimental results and MINEQL+ outputs, the effects of the inhibitors (phosphate and Zn) on precipitation of $CaCO_3$ were evaluated, and possible application of these inhibitors for the Meherpur Paurashava water supply system was assessed.

1.4 Organization of the Thesis

This thesis is presented in five Chapters. The contents of each chapter are summarized below.

Chapter 1: This introductory chapter presents the background and objectives of the study. It also presents outline of methodology followed in this study.

Chapter 2: This chapter presents literature review covering background information on formation, thermodynamics, kinetics and precipitation of calcium carbonate. Common methods employed for addressing the calcium carbonate scaling problem and their potential application in drinking water treatment have also been discussed.

Chapter 3: This chapter describes the methodology followed in this research, including experimental setup used to carry out the laboratory experiments. Furthermore, this chapter describes the analytical methods used for measurement of different parameters.

Chapter 4: This chapter presents an assessment of inhibition potential of Phosphate and Zinc under varying experimental conditions. Effects of the inhibitor (i.e., phosphate and zin) dose, time and degree of supersaturation of water on calcium carbonate precipitation have been analyzed and presented in this chapter. A comparison between the effectiveness of the two inhibitors used is also presented. It also presents the outputs of MINEQL+ simulation of the experimental systems in an effort to understand the speciation of the experimental systems under “equilibrium condition”. Based on the experimental results, it also presents a discussion on the possible application of Phosphate and Zinc for inhibition of precipitation of $CaCO_3$ in the context of Bangladesh.

Chapter 5: This final chapter summarizes the major conclusions from the present study. It also presents recommendations for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The overall objective of the research was to assess the effectiveness of phosphate and zinc as scale inhibitor in delaying precipitation $CaCO_3$ in water containing high concentrations of calcium and carbonate. This chapter presents a review of previous research works conducted in areas relevant to the thermodynamics, kinetics and inhibition of precipitation of Calcium Carbonate ($CaCO_3$) in the water supply systems. In addition, it describes the current scaling problem in the Meherpur Paurashava of Bangladesh.

2.2 Calcium Carbonate: Thermodynamics, Kinetics and the Role of Additives

2.2.1 Thermodynamics

Calcium carbonate is found in various polymorphs [16]. In order of increasing solubility, these polymorphs are calcite, aragonite, vaterite and amorphous calcium carbonates. The solubility products of calcite, aragonite and vaterite are $10^{-8.4}$, $10^{-8.2}$ and $10^{-7.9}$ respectively at 30°C and the solubility decreases at higher temperatures [17]. Various amorphous Calcium Carbonates such as amorphous calcium carbonate and calcium carbonate monohydrate have solubility products $10^{-6.5}$ and $10^{-7.2}$ respectively at 30°C [18-19]. Under normal conditions, calcite is the thermodynamically stable form which will subsequently ripen to form calcite, but at a high degree of supersaturation other less stable polymorphs will form initially. [20-23].

2.2.2 Kinetics

Calcium carbonate precipitation from supersaturated solutions reduces the permeability and porosity in reservoir rocks, the efficiency of water softening devices, and clogs the piping of residential and commercial water systems. In order to minimize scaling problem both in residential and industrial level, the kinetics of calcium carbonate precipitation need to be well learnt [24].

pH, pCO_2 and $[Ca^{+2}]$

The dominant factors influencing calcium carbonate precipitation includes $[Ca^{2+}]$ in solution [25], CO_2 loss [26], and pH [27]. The dissolved CO_2 content in groundwater is 10 to 100 times greater than atmospheric levels [28]. As CO_2 escapes from the system during the experimental crystallization of calcium carbonate, pH of the system decreases [29-30]. Theoretically, one mole of CO_2 should be released for every mole of calcium carbonate precipitated [31]. The pH of a solution can be used to estimate the amount of calcium carbonate precipitated from solution. Degree of saturation in solution, with respect to calcite, can also influence calcium carbonate crystallization in aqueous systems [25, 30, 32-35]. Also, conductivity can be used to measure the relative change in concentration of $[Ca^{+2}]$ over time. Gómez-Morales et al. [33] were able to measure induction times of calcite crystallization using pH and $[Ca^{+2}]$, but found that compared to pH, $[Ca^{2+}]$ does not induce crystallization that much. Unlike Ca^{2+}, concentration of CO_3^{2-} in water is a strong function of pH. With the increase of pH, CO_3^{2-} concentration in water increases rapidly.

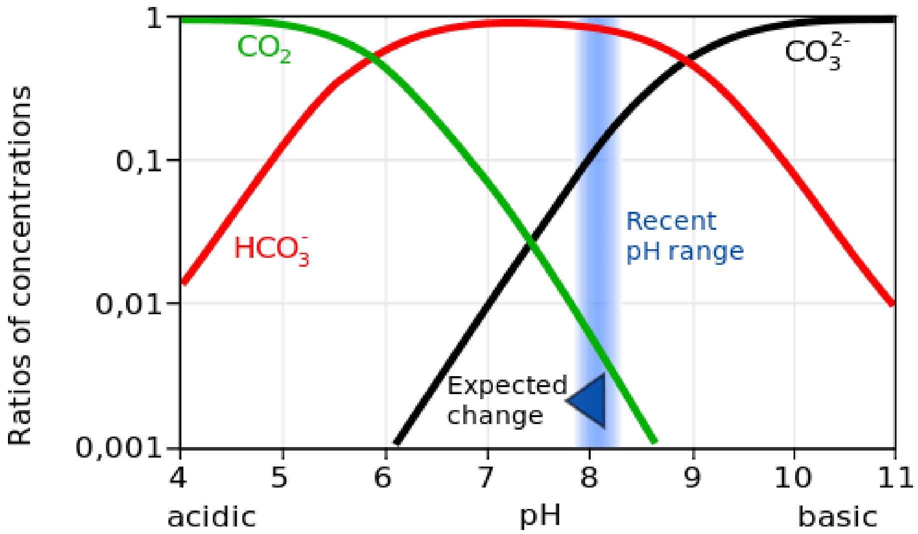


Figure 2.1: Relationship between pH, Ca^{2+}, HCO_3^{2-} and CO_3^{2-} [36]

Calcium Carbonate Polymorphs and Crystal Forms

All three polymorphs of calcium carbonate (i.e. calcite, aragonite, and vaterite) can be produced in the laboratory. However, the most commonly occurring polymorph is calcite [37]. Swinney et al. [38] determined from experiments that by the precipitation of calcite hard water can be soften more effectively rather than aragonite; vaterite was never observed. Both the precipitation rates of the polymorphs of calcium carbonate and the transformation rates from one polymorph to another have to be considered. The dissolution of polymorphic transformation parent phase(s), aragonite or vaterite, causes the growth of the more stable phase which is calcite [21].

Calcium Carbonate Crystal Growth

The first and most common way for growth of calcium carbonate crystal is with the addition of calcite seed crystals where seed crystals act as nucleation sites for crystallization from supersaturated solutions. The second method is the spontaneous nucleation of calcium carbonate from supersaturated solutions without addition of any seed crystals. However, the mechanics of calcium carbonate precipitation is appeared to be same for both cases. As extremely high saturation index is required to initiate spontaneous nucleation, it is not ideal for determining calcium carbonate precipitation rate. As there is no crystalline material prior to induced crystallization, it can be applied to estimate the amount of calcium carbonate precipitated from solution. For these reasons the spontaneous nucleation method of precipitating calcium carbonate will not be discussed any further. Seed crystals are usually euhedral, transparent, approximately 10 μm in size [29], and retain their euhedral shapes throughout calcium carbonate growth [39].

Several authors propose that calcium carbonate precipitation in a seeded experiment is surface area controlled [21, 25, 29, 40-41]. Crystal surface area controls the growth rate of calcite which is believed to be proportional to the number of available growth sites [39]. This process may be the rate limiting step for crystal growth of calcite [31, 41].

Calcium Carbonate Precipitation in the Presence of Contaminants

The effect of natural contaminants (e.g., Mg, Mn, Sr, Si, SO_4^{2-}, PO_4^{3-}, and dissolved organic carbon) on the precipitation of calcium carbonate is very important. Among these natural contaminants, Mg [37], Si [30], PO_4^{3-} [42-43] and dissolved organic carbon (DOC) [28] have a significant effect on the rate of calcium carbonate precipitation. DOC and PO_4^{3-} attach to crystal surfaces and reduce the number of potential precipitation sites. Thus, affects crystal growth [25, 28, 42].

Formation of amorphous phase of calcium carbonate occurs prior to crystallization when certain contaminants are present in the solution [37, 44]. Like amorphous shapes and jagged edges were found easily during calcite growth when PO_4^{3-} is present in the solution [25].

Precipitation of calcite crystal occurs from supersaturated solutions when Mg is present but this is preceded by the amorphous calcium carbonate phase convert to crystalline form similar to calcite crystals observed to grow in the absence of Mg. The size of the calcite crystals also appears to be correlated to the number of impurities incorporated within the crystal structure and more impurities yield smaller crystals [44]. Gebauer et al. [45] also observed an amorphous phase before the crystalline phase occurred. They proposed the growth of stable calcium carbonate clusters through the binding of ions. Ca^{+2} and CO^{3-} ions bind together to form an amorphous phase without any crystalline structure which further convert into the most thermodynamically stable calcium carbonate polymorph. All steps associated with ion binding are anticipated to have pH dependency.

Also, precipitation of calcium carbonate polymorphs / crystallization induction rate / polymorphic transformation rate is affected by the contaminants. As example, silica affects precipitation and induction rate the calcium carbonate polymorph [30].

Calcium Carbonate Reaction Rates

It cannot clearly be identified how kinetics and thermodynamics influences in calcium carbonate precipitation. Although initially there is a rapid growth surge of calcium carbonate but eventually it slows down according to kinetic rate equations during calcite precipitation. [40]. The most commonly proposed rate limiting steps are CO_2 production [26, 31], the number of available growth sites [25, 31], system flow characteristics [26] and [Ca^{+2}] saturation levels [25].

According to most researchers, the most important thermodynamic factor is the [Ca^{+2}] in solution, but the most important kinetic factor is still disputable. According to Kamkha et al. [32], pH, specifically the [HCO^{3-}], control the kinetics of calcium carbonate precipitation, but according to Dickinson et al. [35] proposes that the kinetics of the growth reactions were controlled by CO_2 release. The genetic linkage between CO_2 release and [HCO^{3-}] supports both of the postulations.

The most creditable kinetic factor affecting calcium carbonate crystallization is the [Ca^{2+}] in solution. The [Ca^{2+}] with respect to the saturation level within a system significantly affect the growth rates and mechanisms of calcium carbonate. Calcite exhibits two different growth sites even for saturation levels greater than 1 but less than 2. Surface nucleation and coalescence dominates calcite growth at first, but it transits to a mechanism which resembles spiral growth over time. In undersaturated close to equilibrium solutions, both surface dissolution and precipitation of calcium carbonate appear to occur simultaneously [25].

Theoretically, one mole of CO_2 is produced for every mole of calcium carbonate precipitated. Thus, the rate at which CO_2 can be produced and removed from the system can also be a rate limiting step for calcium carbonate precipitation. Aquatic organisms consume CO_2, and that might increase the rate of calcium carbonate precipitation [28]. Dreybrodt et al. [26] studied the effect of enzymes on the reaction rate of 2.1 in order to determine if CO_2 production could be enhanced.

$$HCO^{3-} + H^+ \rightarrow H_2O + CO_2 \quad \ldots \quad \ldots \quad \ldots \quad (2.1)$$

Their observation suggests that this reaction was enhanced when enzymes were present in the system, suggesting a linkage of CO_2 removal and carbonate precipitation. However, the enzymes' exact role remained disputable [31].

Calcium carbonate precipitation in a solution can be affected by one parameter in the simplest system but in more complex systems like natural system, it can be affected by many parameters. For example, in turbulent flow systems concentration gradients form in a limited level, thereby they homogenize the surface fluid chemistry near the crystal surface and directly affect the calcium carbonate precipitation rate. But in some studies, a quasi-equilibrium phase prior to true chemical equilibrium was observed which complicates the procedure. The quasi-equilibrium represents the change in slope of the concave parabolic curve of [Ca^{2+}] in solution with time. Initially, [Ca^{2+}] in solution decreases very rapidly over time, but eventually it slows down. This equilibrium is maintained for a substantial period of time until the system reaches true chemical equilibrium [26].

As we compare the results of different studies, it can be realized that calcium carbonate precipitation rate laws need to be chosen and applied carefully [34]. Deriving precipitation rate laws just cannot be done by analyzing the change in bulk chemistry of a system as there are discrepancies between rate law equations from different studies based on different scales. For example, Goodarz-nia and Motamedi [39] observed an interesting phenomenon during their experimental precipitation of calcium carbonate which was not noted in any other study was that when calcium carbonate precipitates, the overall crystal size increased with time until around 50 minutes after initial precipitation. After this period, the crystal sizes were decreased instead of further increasing. This phenomenon could not be explained. But plausibility is this could have been due to the system reaching equilibrium, achieving slightly undersaturated conditions, or system transforming from one polymorphous phase to another with lower equilibrium solubility values.

Experiments have been made on the influence of water composition, temperature and water pH on the calco-carbonic system ($CaCO_3$-CO_2-H_2O) to assess their effects towards $CaCO_3$ precipitation [46-47]. Solution needs to be supersaturated in order to occur crystallization, but only supersaturation is not adequate to induce crystallization. This requires nucleation sites in the form of seeds, embryos or foreign matter in the solution. Although nucleation is the controlling step, with the formation of the critical nuclei, the crystallization proceeds and growth and re-crystallization occurs [48].

The chemical reaction of $CaCO_3$ precipitation is:

$$Ca^{2+} + HCO^{-} + OH^{-} \Leftrightarrow CaCO_3(s) + H_2O \quad \ldots \quad \ldots \quad \ldots \quad (2.2)$$

Or,

$$Ca^{2+} + 2HCO^{-} \Leftrightarrow CaCO_3(s) + CO_2(g) + H_2O \quad \dots \quad \dots \quad \dots \quad (2.3)$$

The solubility product (K_{sp}) of each form varies with temperature. $CaCO_3(s)$ has significantly lower solubility at higher temperatures; thus, high precipitation occurs as temperature rises.

$$K_{sp} = [\,Ca^{2+}\,]\,[\,CO_3^{2-}\,] \quad \dots \quad \dots \quad \dots \quad (2.4)$$

2. 3 Overview of $CaCO_3$ from source to consumers

$CaCO_3$ formation has both positive and negative effects from source to consumers. (1) Source water: Surface water is associated with CO_2 which can control pH and also add inorganic carbon to the system. Phosphate and Natural Organic Matter (NOM) can be added to water with runoff or wastewater discharge, while calcium containing minerals in soils such as limestone can dissolve in water. These can act as natural inhibitor to calcium carbonate precipitation. (2) Water treatment plant: Corrosion inhibitors also act as antiscalants which can inhibit $CaCO_3$ precipitation. Softening processes often scale and produce a brine reject stream with higher hardness and treated water with lower hardness. (3) Distribution system: $CaCO_3$ precipitates in the distribution lines which have the capability of protecting the pipes from corrosive waters and potentially repairing leaks but this results in increase of head loss of the system. (4) Premise plumbing: In residential buildings which have ion exchange or Reverse Osmosis (RO) membrane softeners, brine reject streams with high hardness are produced. As water heaters are very susceptible to scaling due to their high temperatures, precipitation of calcium carbonate can easily coat heating elements and clog the narrow channels of water heaters. Particulate $CaCO_3$ may accelerate erosion. [6]

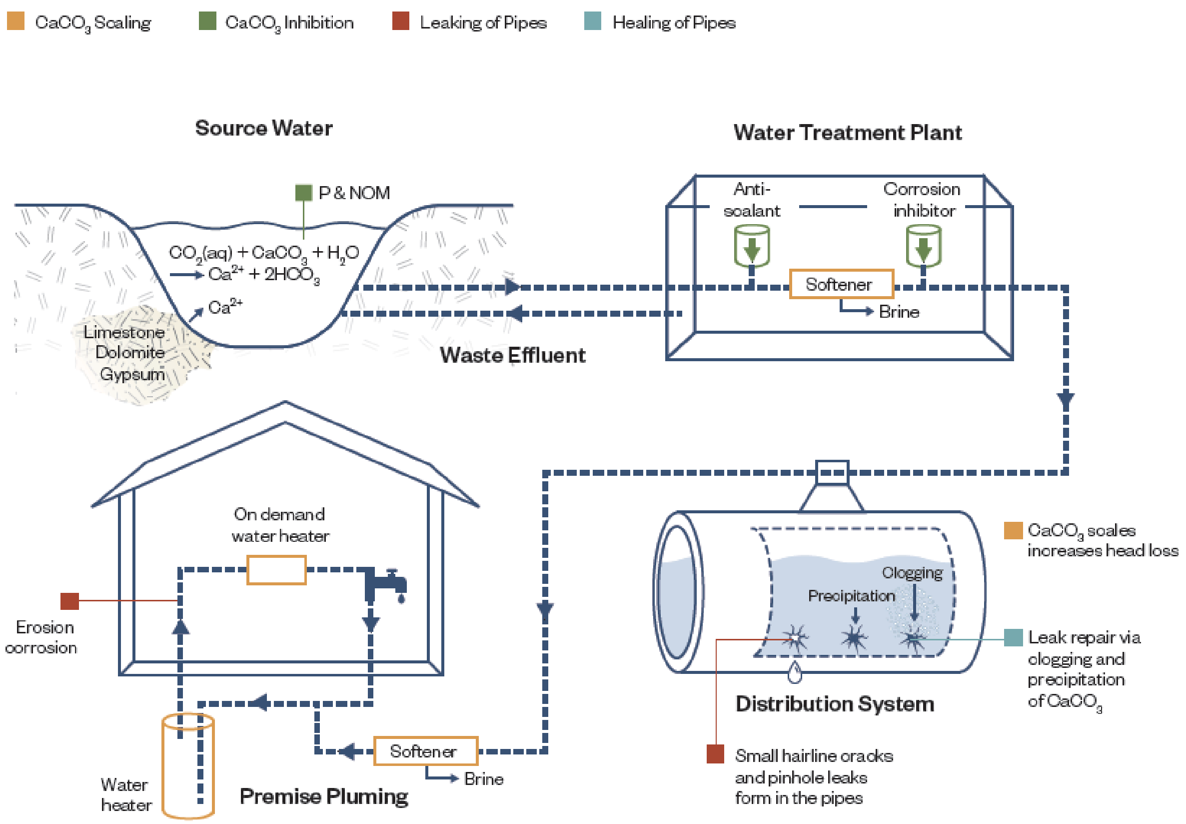


Figure 2.2: Overview of $CaCO_3$ from source to consumers [6]

2.4 Scaling Problem

$CaCO_3$ scaling is a problem in granular media filters but it can bind together the filter bed making it difficult to regenerate the media [49]. This is also a major issue in modern filter systems like Reverse Osmosis (RO) or ultrafiltration membranes as it causes membrane fouling [50]. The dissolved Ca^{2+} and inorganic carbon in the reject stream can result in precipitation of calcium carbonate on the membrane surface [51] and feed water pH is to be lowered to prevent scaling on the membrane and brine discharge system [52].

The increased propensity of $CaCO_3$ to precipitate at higher temperatures makes scaling a troublesome issue especially in water heater or cooler applications in which precipitated $CaCO_3$ erupts heat transfer and system efficiency. Water heating is extremely energy intensive and the energy demand for heating might exceed the energy demand for entire water and wastewater utility sector of a building system [53]. Hard water can lower the heat transfer efficiency of gas storage water heaters by 8.5%, and of instantaneous gas water heaters by 30% if no softening or de-liming is practiced over a 15 year lifecycle. That is why softening process is applied which can reduce the life cycle cost of instantaneous gas water heaters by 22.5% and gas storage water heaters by 6.6% over a 15 year lifecycle [54].

2.5 Recent Trends Affecting $CaCO_3$ Formation

In the last decades, the potable water treatment and distribution has changed remarkably that can profoundly change the extent of $CaCO_3$ formation and scaling in plumbing systems (Figure 2.2). Inorganic carbon (as carbonate) dissolves into natural water systems from CO_2 in the atmosphere, and Ca^{2+} is released in natural waters through dissolution of minerals that come into contact with the water such as portlandite, gypsum, and dolomite (Table 2.1). In regions where calcium chloride is used, thousands of tons of Ca^{2+} can be added to groundwater from de-icing salt [55].

Table 2.1: Solubility of calcium containing minerals found in natural waters [6]

Mineral	**pK_{sp} (25°C)**	**Reaction**
Limestone (calcite + aragonite)	8.34 -8.48	$CaCO_3$ (s) $\rightleftharpoons Ca^{2+} + CO_3^{-}$
Portlandite	22.8	$Ca(OH)_2$ (s) $\rightleftharpoons Ca^{2+} + 2OH^-$
Dolomite	17.2	$CaMg(CO_3)_2$ (s)+ $H^+ \rightleftharpoons$ $MgCO_3$ (s) + $Ca^{2+} + HCO_3^-$
Gypsum	4.16	$CaSO_4.2H_2O$ (s) $\rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$

$CaCO_3$ scaling in heating systems has recently become a great concern. Higher hot water system temperature is targeted (> 51 °C) to reduce growth of pathogens (e.g., Legionella pneumophila). Solubility of $CaCO_3$ decreases as temperature increases. As a result, rates of precipitation also increase and scale formation occurs on the surface of the heating element and throughout the system more rapidly. This can cause serious problems including loss of heat transfer efficiency in heating systems, head loss (energy loss) induced by pipe clogging, and in some cases erosion corrosion from particles [8,56 – 58]. Low heat transfer efficiency can severely hamper the operation of water heaters in homes and buildings, cooling towers and heat exchangers in industrial settings [5].

2.6 Temperature Dependence of Solubility

Calcium level in Natural water is affected by rising CO_2 level in the atmosphere and prolonged droughts due to global warming [59-60]. As seen from Figure 2.3, the $CaCO_3$ saturation index in drinking water system is rising with the atmospheric CO_2 level. Higher CO_2 level and increased temperature contributes to the dissolved organic carbon in the water [61], which contrarily inhibits $CaCO_3$ formation. The overall effect of climate change induced increase in temperature on $CaCO_3$ precipitation is thus still unclear [6].

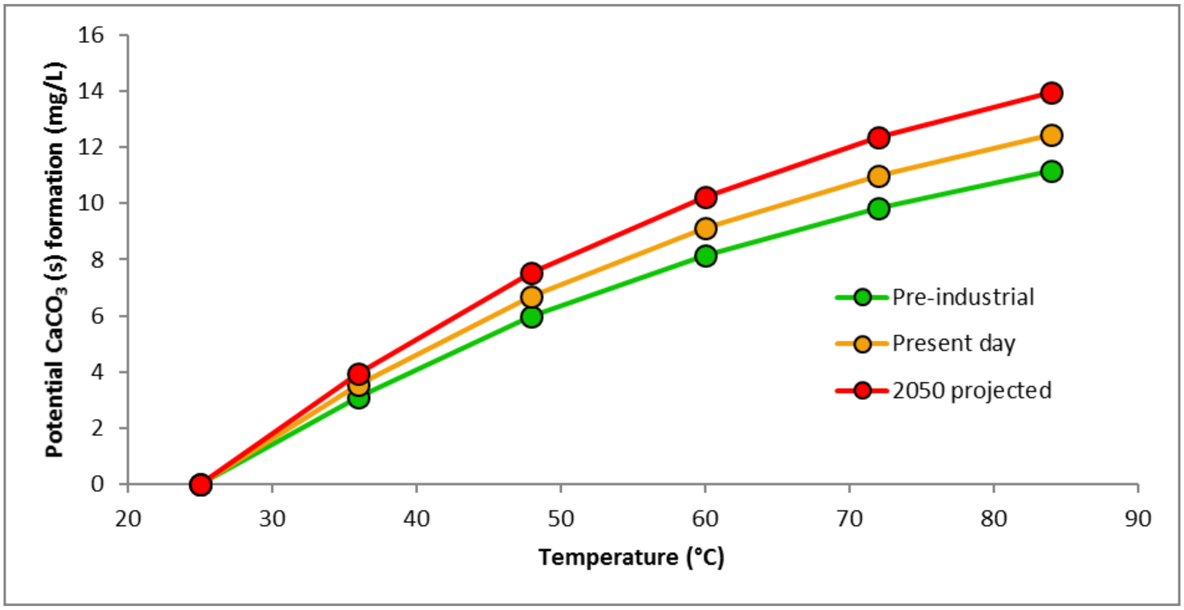


Figure 2.3: Impact of temperature increase on $CaCO_3$ formation due to the rise of atmospheric CO_2 level [6]

Table 2.2: Temperature dependence of solubility product for $CaCO_3$ polymorphs [6]

Polymorph	**pK_{sp} (25 °C)**	**K_{sp} Equation**	**Temperature Range (°C)**
Amorphous Calcium Carbonate (ACC)	6.04	logKsp = 1247/T − 10.224	16 to 60
Vaterite	7.91	logKsp=−172.1295−0.077993*T + (3074.688)/T + 71.595 * logT	0 to 90
Aragonite	8.34	logKsp = −171.9773 − 0.077993 ∗ T + (2903.293)/T + 71.595 * T	0 to 90
Calcite	8.48	logKsp = −171.9065 − 0.077993 ∗ T + (2839.319)/T + 71.595 *T	0 to 90

Note: T is temperature in K.

$CaCO_3$ crystals consists of Ca^{2+} and CO_3^{2-} lattice ions, both of which are abundant in natural water. Different polymorphs of $CaCO_3$ has different temperature dependent solubility product (Ksp). As seen in Table 2.2, amorphous phase (ACC) of $CaCO_3$ has the smallest pKsp (-log(Ksp)) at room temperature, which translates to the highest solubility in water. On the other hand, at room temperature vaterite, aragonite and calcite have decreasing solubility in the order they are listed here. In all cases, $CaCO_3$ solubility is negatively affected by the increase in temperature, making the precipitation problem severe in hot water system [6].

Saturation index and formation of $CaCO_3$

Ca^{2+} levels found in ground waters are governed by regional geological conditions ie. existence of limestone, dolomite, etc. in the soil [6]. On the other hand, water pH level could make CO_3^{2-} the dominant form of carbon compounds in the water, as evident from pK_a values of the reactions below [17].

$$CO_2(g) + H_2O \rightleftharpoons CO_2\,(aq) + H_2CO_3(aq) \qquad pK_H = 1.47$$

$$H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^-(aq) \qquad pK_{a1} = 6.4$$

$$HCO_3^-(aq) \rightleftharpoons H^+ + CO_3^{2-}(aq) \qquad\qquad pK_{a2} = 10.3$$

The ion activity product Q for $CaCO_3$ is defined by the product of Ca^{2+} and CO_3^{2-} activities, as-

$$Q = \{Ca^{2+}\}\{CO_3^{2-}\} \quad \ldots \quad \ldots \quad \ldots \quad (2.5)$$

For undersaturated solution, $Q < K_{sp}$ and precipitation is thermodynamically unfavorable. On the contrary, $Q > K_{sp}$ leads to supersaturated solution and $CaCO_3$ precipitation can occur.

In a supersaturated solution, the precipitation process starts with nucleation. When no other crystals are present in the system, nucleation can be spontaneous or can be induced by any foreign particle (primary nucleation). Induced nucleation, also termed as heterogenous nucleation [62] is the main pathway for $CaCO_3$ precipitation. Foreign solids induce nucleation by lowering the activation energy for the process [63]. Once initial crystals are formed further $CaCO_3$ growth happens through secondary nucleation process [62] on the pre-existing crystals.

The time it takes for a supersaturated solution to initiate $CaCO_3$ precipitation, i.e., the induction time (τ), is expressed as [64]-

$$\tau = K\,(\Omega^{0.5} - 1)^p \quad \ldots \quad \ldots \quad \ldots \quad (2.6)$$

Here, K = system dependent parameter

p= apparent growth order, typically 8.0 for $CaCO_3$ [64]

$\Omega = \frac{Q}{k_{sp}}$ = degree of supersaturation

In the absence of impurities, τ could vary from <1 to 136 minutes [64] depending on the degree of saturation of $CaCO_3$ in the water.

2.7 Precipitation and Growth in Plumbing and Distribution Systems

As indicated in the section above, heterogeneous nucleation is statistically more probable than its homogeneous counterpart where no significant foreign particles are present in the solution. Therefore, homogeneous nucleation only becomes apparent when degree of supersaturation exceeds 1.6 [65]. The Mechanism for homogeneous nucleation of $CaCO_3$

follows classical nucleation theory (CNT), according to which a nucleus gets stabilized when a critical radius is achieved equalizing bulk and surface energies of the nuclei [66]. According to recent research, pre-nucleation clusters (PNCs) are responsible for $CaCO_3$ precipitation [45]. PNCs contain $CaCO_3$ lattice ions that are at a mixed phase state with the solution. Characteristics of PNCs also dictates which polymorph of $CaCO_3$ would nucleate. Stable PNCs tend to yield calcite while less stable PNCs yield vaterite polymorphs [66-67].

Ostwald's rule of stages roughly governs the process of homogeneous $CaCO_3$ precipitation, which states that least stable polymorph crystallizes before it could transform into the most stable form [68]. Among $CaCO_3$ polymorphs, at low temperature (sub 30 °C) ACC precipitates first, then vaterite follows and next calcite, the most stable form, is produced [69-70]. At elevated temperatures (above 60°C), ACC transitions to aragonite first and then to calcite. At intermediate temperatures, $CaCO_3$ crystallization is more closely governed by Ostwald's rule and every polymorph is formed and eventually they transform into calcite [70].

Scales formed in plumbing and distribution systems most like originates from heterogeneous nucleation. Already present scales or bare pipe surfaces that lower the energy barrier aids heterogenous nucleation in the plumbing system. Plumbing surface materials characteristics like surface roughness and surface charge affects heterogeneous precipitation of $CaCO_3$ [71-74]. Inert materials like polymers are less prone to scale compared to metallic surfaces [75]. Among metals, Study on copper, steel and aluminum surfaces revealed that copper induces the highest amount scaling [74]. When copper and polypropylene tubes are compared, copper experienced twice as much scaling with Ca-containing minerals [76]. Comparison between PVC and stainless steel surfaces indicates that the latter one has higher precipitation rate at lower Ca^{2+} concentration (i.e. 200 mg/l), however at higher concentration (i.e. 400 mg/l) the trend reverses [46]. However, not much data available on how heterogeneous nucleation is affected by more traditional water materials like concrete and cast iron.

2.8 Control and Prevention of Calcium Carbonate Scaling

If the presence of significant $CaCO_3$ scaling is confirmed in the distribution system, various control and preventive measures could be undertaken to mitigate that. Based on the infrastructure and environmental consideration, the mitigation steps could be active or passive.

As an active step, complete prevention of scaling could be achieved using scale inhibitors. Scale inhibitors are add-on chemicals to the drinking water that delays or prevents $CaCO_3$ precipitation completely. Common scale inhibitors for industrial water systems include phosphonates, phosphate esters, polyacrylates and phosphates [6]. For household drinking water system, only the latter one could be used.

Magnesium cation (Mg^{2+}), a commonly present inorganic element in the drinking water, could act as a scale inhibitor. By getting absorbed onto the active calcite growth site, Mg^{2+} prevents any further $CaCO_3$ accumulation [14]. Added Mg^{2+} concentration of 10^{-3} M can successfully stimulate this inhibition process [77]. Among other inorganic cations, Zn^{2+} addition can also inhibit calcite formation when added at a concentration of 10^{-7} M [11].

Phosphates and some natural organic acids are also widely used as scale inhibitors in drinking water system. When added at a concentration of 10^{-8} M or above, various phosphate derivatives like orthophosphate, pyrophosphate, triphosphate and hexametaphosphate can block calcite formation [6, 12, 78]. Natural organic acids like fulvic and humic acid can also inhibit calcite formation in the drinking water systems [79,80]. Organic acids prevent $CaCO_3$ formations locally near the point of addition, whereas when supersaturated with phosphates the calcification could be prevented to an extended distance [81-82].

Calcite formation could be controlled by stabilizing metastable polymorphs of $CaCO_3$ like aragonite, vaterite and ACC [6]. Zn^{2+} ion, when added to the drinking water can prevent calcite formation, as mentioned previously, by favoring aragonite nuclei formation. Once aragonite nuclei are formed Zn^{2+} gets absorbed on to the active crystal sites and prevents any further $CaCO_3$ growth [10].

In addition to the scale inhibitors, there are some passive methods of preventing $CaCO_3$ scaling by controlling water temperature and pH. Lower water temperature can decrease precipitation either by increasing solubility of $CaCO_3$ polymorphs or by slowing down the reaction kinetics of calcite formation [83-84]. Also, lower temperature could make scale inhibitors like polyphosphate more effective [6]. On the other hand, reduction of the water pH and removal of the dissolved Ca can also lead to less $CaCO_3$ formation [6]. However, controlling water physical properties to prevent calcite formation has its downfall as it can lead to pathogen growths or, cause corrosion of the metallic pipelines [85]. Other passive methods include, controlling the water pipe surface materials and roughness. Surface roughness of the pipe can affect the porosity and tensile strength of the calcite scales and might help prevent large scale $CaCO_3$ accumulation or make the removal process simpler [71].

2.9 Present Scenario of Bangladesh in Meherpur Paurashava

Meherpur Paurashava is suffering from high concentration of Hardness (Ca and Mg) in the groundwater used for supply of potable water. Available data suggests that the existing WTP (designed as IRP) at the Paurashava is able to remove Fe and Mn from raw groundwater. However, as pH increases after withdrawal of groundwater (due to escape of dissolved carbon-di-oxide), Ca begins to precipitate as Calcium Carbonate ($CaCO_3$), forming crusts in distribution system and plumbing fixtures. This is causing serious problem for the Paurashava and its citizens. Calcite encrustation is causing clogging of distribution network, head loss, and damaging plumbing fixtures. Figure 2.8 and 2.9 shows photographs of scales from in water distribution pipes and pieces of scale collected from a household. From available data on raw water quality at Meherpur WTP [7], Calculated degree of supersaturation ($\Omega = Q/K_{sp}$) for Meherpur water varies from 8.77 to 25.3.

Figure 2.4: Scaling in pipes at Meherpur WTP [7]

Figure 2.5: Scaling collected from households in Meherpur [7]

It is therefore very important to carry out research work on prevention and control of $CaCO_3$ precipitation in water supply and distribution system in Bangladesh.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The main objective of this research was to develop better understanding of the effectiveness of two inhibitions - Phosphate (PO_4^{3-}) and Zinc (Zn^{2+}) - in preventing or delaying precipitation of Calcium Carbonate ($CaCO_3$). This objective was achieved through carrying out a series of batch experiments where effectiveness of PO_4^{3-} and Zn^{2+} as inhibitors was assessed in both 0.1 M NaCl solutions and groundwater samples. This Chapter presents the experimental setup and methods used in this research to carry out the laboratory experiments. Furthermore, this chapter describes the analytical methods used for measurement of different water quality parameters.

3.2 Batch Experiments

In order to evaluate the precipitation of $CaCO_3$ in the presence of PO_4^{3-} and Zn^{2+}, batch experiments were carried out under a range of conditions. For each inhibitor (i.e., phosphate or zinc), experiments were carried out to evaluate the effect of inhibitor concentration, mixing time, and degree of super-saturation. At first batch experiments were conducted in 0.1 M NaCl solutions (in deionized water), in order to eliminate possible effects of constituents that could interfere with $CaCO_3$ precipitation (e.g., Mg^{2+}, silica). Subsequently, similar batch experiments were carried out with natural groundwater.

For all batch experiments in 0.1 M NaCl, concentrations of Ca and carbonate in solution were varied to achieve the desired initial concentration and/or degree of saturation (Ω). Reagent grade $CaCl_2$ and $NaHCO_3$ were used to prepare stock solutions of Ca and carbonate/bicarbonate, respectively, which were used to achieve the required concentrations of Ca and carbonate in water (and thus required Ω). Concentrations of H_2CO_3, HCO_3^- and CO_3^{2-} were estimated based on the measured concentration of total alkalinity and pH of the solutions. Phosphate stock solution, for amending the experimental solutions with phosphate, was prepared using reagent grade potassium di-hydrogen phosphate; zinc stock solution, for amending the experimental systems with Zn, was prepared using reagent grade $ZnCl_2$ solution.

A stock solution of 11.7 g/L of NaCl was prepared for the preparation of 0.1 M NaCl solutions. To stock solution of 6.72 g/L $NaHCO_3$ was used for spiking the solution with carbonate. Stock solutions of $CaCl_2$ were prepared at two different concentrations; 4.1625 g/L.

3.2.1 Batch Experiments in 0.1 M NaCl Solution with Phosphate as Inhibitor

At first, effect of the inhibitors (i.e., phosphate and Zn) have been evaluated in batch experiments carried out 0.1 M NaCl solution in deionized water (instead of groundwater), in order to eliminate possible effects of constituents that could interfere with $CaCO_3$(s) precipitation (e.g., Mg^{2+}, silica). For each batch experiment, a 200 ml volumetric flask was taken, to which about 100 ml of deionized water was added. Then required quantities of NaCl stock solution, $CaCl_2$ stock solution, $NaHCO_3$ stock solution, and phosphate stock solution were added to the flask to achieve the desired concentrations Ca, carbonate, and phosphate concentrations. Then additional deionized water was added to the flask to make to total volume exactly 200 ml. As noted earlier, all experiments were carried out in 0.1 M NaCl. For batch experiments carried out to assess the effect of phosphate concentration on precipitation of $CaCO_3$, initial Ca concentration was fixed at 75 mg/l, and total alkalinity values were kept at about 200 mg/l as $CaCO_3$; total alkalinity values were measured for each set of experiments. The contents of the volumetric flask were immediately transferred to a 250 ml beaker, and the beaker was subjected to stirring using a magnetic stirrer (for a specified period of time). For these experiments, mixing time was fixed at 30 minutes; as discussed below, mixing time was varied in subsequent experiments to assess the effect of mixing time on $CaCO_3$ precipitation. Phosphate concentrations in these experiments were varied from 0 to 5 mg/l; a total of 10 (ten) batch experiments were carried out for initial Ca concentration of 75 mg/l and mixing time of 30 minutes, where phosphate concentrations were as follows: 0 mg/l, 0.10 mg/l, 0.25 mg/l, 0.50 mg/l, 0.75 mg/l, 1.0 mg/l, 2.0 mg/l, 3.0 mg/l, 4.0 mg/l and 5.0 mg/l. For each batch experiment, at the end of the mixing period, about 50 ml water sample was collected from each beaker and was filtered through a 0.45 µm filter cartridge (UNIFLO 25 mm Nylon Syringe Filters) in order to filter out any precipitated $CaCO_3$(s). The supernatant was then analyzed for dissolved Ca concentration. Concentrations of total hardness as well as Ca (using an AAS) were measured. A higher dissolved Ca concentration suggested lower precipitation of $CaCO_3$ and vice versa. The pH and temperature of the solution in each beaker were also measured at the end of the experiment. Average pH and average temperature of these 10 sets of experiments were 8.31 and 26.6 °C, respectively.

Additionally, similar experiments were carried out to assess the effect of mixing time on precipitation of $CaCO_3$(s). These experiments were similar to the experiments described above, but here the mixing times were: 30 minutes; 1 hour; 3 hours and 5 hours. For each mixing time, phosphate concentration was varied from zero to 5 mg/l (using 10 different phosphate concentrations as noted above). Thus, an additional 30 batch experiments were carried out in order to assess the effect mixing time on precipitation of $CaCO_3$. Data generated from these experiments were also used to evaluate the effect of phosphate concentration on precipitation of $CaCO_3$(s) over longer periods of time.

Finally, batch experiments were conducted to evaluate the effect of the degree of super-saturation of water on the precipitation of $CaCO_3$(s) in the presence of phosphate. For this purpose, calcium (Ca) and carbonate concentrations were varied in water in order to achieve different degree of super-saturation in water. Degree of super-saturation is defined as $\Omega = Q/K_{sp}$, where Q actual product of the activities of calcium and carbonate = $[Ca^{2+}]\ [CO_3^{2-}]$, and K_{sp} is the solubility product for $CaCO_3$(s). If $\Omega < 1$, the solution is under saturated, while if $\Omega > 1$, the solution is super saturated. Table 3.1 shows the composition of solutions used to evaluate the effect of degree of super-saturation on the precipitation of $CaCO_3$(s). As shows in Table 3.1, Ca concentration in these experiments were varied from 75 to 200 mg/l, and calculated degree of super-saturation (Ω) varied from 11.87 to 171.42.

Table 3.1: Composition of solution in the batch experiments carried out to assess the effect phosphate on precipitation of $CaCO_3$(s) for different degrees of super-saturation

Expt. No.	Average pH	Average Temp (°C)	Ca^{2+} (mg/l)	CO_3^{2-} (calculated) (mg/l)	Calculated Ω
1	8.06	24.7	75	1.36	11.87
2	8.31	22.86	100	2.41	26.49
3	8.16	25.31	150	1.71	30.40
4	8.80	25.67	200	7.13	171.42

For each of the four solution compositions listed in Table 3.1, batch experiments were carried out (similar to the way described above) where phosphate concentrations were varied from 0 to 5 mg/l (in 10 different phosphate concentrations); a mixing time of 30 minutes was used in these experiments. Thus, a total of 40 batch experiments were carried out to assess the effect of the degree of super-saturation on precipitation of $CaCO_3$(s) in the presence of phosphate as inhibitor.

MINEQL+ simulations were carried out to understand the speciation of chemical constituents in the experimental systems under "equilibrium" conditions. The simulations were carried out for the following conditions: $(Ca)_T = 1.875 \times 10^{-3}$M (= 75 mg/l)

$(Na)_T = 0.10$ M
$(Cl^-)_T = 0.10$ M
pH = 8.06
Alkalinity = 4.0 meq/L (= 200 mg/l as $CaCO_3$) ("closed system" considered)
$(PO_4^{3-})_T = 0$ to 5.21×10^{-5} M (0 to 5 mg/l)

3.2.2 Batch Experiments in 0.1 M NaCl with Zinc as Inhibitor

In order to evaluate the effect of Zn as an inhibitor, batch experiments were carried out following the methodology described above. For each batch experiment, a 200 ml volumetric flask was taken, to which about 100 ml of deionized water was added. Then required quantities of NaCl stock solution, $CaCl_2$ stock solution, $NaHCO_3$ stock solution, and Zinc stock solution were added to the flask to achieve the desired concentrations Ca, carbonate, and Zn concentrations. Then additional deionized water was added to the flask to make to total volume exactly 200 ml. For evaluating the effect of Zn concentration on precipitation of $CaCO_3$(s), initial Ca concentration was fixed at 75 mg/l. The contents of the volumetric flask were immediately transferred to a 250 ml beaker, which was subjected to stirring in a magnetic stirrer for 30 minutes. Zinc (Zn) concentrations in these experiments were varied from 0 to 5 mg/l in 10 different concentrations as follows: 0 mg/l, 0.10 mg/l, 0.25 mg/l, 0.50 mg/l, 0.75 mg/l, 1.0 mg/l, 2.0 mg/l, 3.0 mg/l, 4.0 mg/l and 5.0 mg/l. At the end of the mixing period, about 50 ml water sample was collected from each beaker and was filtered through a 0.45 µm filter cartridge (UNIFLO 25 mm Nylon Syringe Filters) in order to filter out any precipitated $CaCO_3$(s). The supernatant was then analyzed for dissolved Ca concentration. Concentrations of total hardness as well as Ca (using an AAS) were measured. The pH and temperature of the solution in each beaker were also measured at the end of the experiment. Average pH and average temperature of these 10 sets of experiments were 7.53 and 20.9 °C, respectively.

Additionally, similar experiments were carried out to assess the effect of mixing time on precipitation of $CaCO_3$(s) in the presence of Zn. These experiments were similar to the experiments described above, but here the mixing times were: 30 minutes; 1 hour; 3 hours and 5 hours. For each mixing time, Zn concentration was varied from zero to 5 mg/l using 10 different Zn concentrations. Thus, an additional 30 batch experiments were carried out in order to assess the effect mixing time on precipitation of $CaCO_3$. Data generated from these experiments were also used to evaluate the effect of Zn concentration on precipitation of $CaCO_3$(s) over longer periods of time.

Finally, batch experiments were conducted to evaluate the effect of the degree of super-saturation of water on the precipitation of $CaCO_3$(s) in the presence of Zn. For this purpose, calcium (Ca) and carbonate concentrations were varied in water in order to achieve different degree of super-saturation in water. Table 3.2 shows the composition of solutions used to evaluate the effect of degree of super-saturation on the precipitation of $CaCO_3$(s). As shows in Table 3.2, Ca concentration in these experiments were varied from 75 to 200 mg/l, and calculated degree of super-saturation (Ω) varied from 3.10 to 10.06.

For each of the four solution compositions listed in Table 3.2, batch experiments were carried out (similar to the way described above) where Zn concentrations were varied from 0 to 5 mg/l (in 10 different phosphate concentrations); a mixing time of 30 minutes was used in these experiments. Thus, a total of 40 batch experiments were carried out to assess the effect of the degree of super-saturation on precipitation of $CaCO_3$(s) in the presence of Zn as inhibitor.

Table 3.2: Composition of solution in the batch experiments carried out to assess the effect Zn^{2+} on precipitation of $CaCO_3$(s) for different degrees of super-saturation

Expt. No.	Average pH	Average Temperature (°C)	Initial Ca^{2+} (mg/L)	Initial CO_3^{2-} (calculated) (mg/L)	Solubility Product, k_{sp}	Calculated Ω
1	7.53	20.9	75	0.347	3.49×10^{-9}	3.10
2	7.59	22.1	100	0.407	3.44×10^{-9}	4.93
3	7.51	21.6	150	0.337	3.46×10^{-9}	6.08
4	7.56	24.3	200	0.404	3.35×10^{-9}	10.06

Notes: (1) All experiments were carried out in 0.10 M NaCl solution;

(2) Mixing time in all experiments = 30 minutes

MINEQL+ simulations were carried out to understand the speciation of chemical constituents in the experimental systems under "equilibrium" conditions. The simulations were carried out for the following conditions: $(Ca)_T = 1.875 \times 10^{-3}$M (= 75 mg/l)

$(Na)_T = 0.10$ M

$(Cl^-)_T = 0.10$ M

pH = 8.06

Alkalinity = 4.0 meq/L (= 200 mg/l as $CaCO_3$) ("closed system" considered)

$(Zn)_T = 0$ to 7.65×10^{-5} M (0 to 5 mg/l)

3.2.3 Batch Experiments with Natural Groundwater Samples

Batch experiments were carried out with natural groundwater in order evaluate the ability of Zn and phosphate inhibitors to delay or inhibit precipitation of $CaCO_3$(s) under normal condition. For this purpose, groundwater samples were collected from a deep tubewell (DTW) pump station near DSW office at BUET (before chlorination). The samples were immediately analyzed for a wide range of parameters, including Electrical Conductivity (EC), pH, Temperature, Hardness, Alkalinity, Chloride (Cl^-), Phosphate (PO_4^{3-}), Silica (SiO_2), Zinc (Zn^{2+}), Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Nickel (Ni^{2+}), and Copper (Cu^{2+}). Table 3.3 shows the characteristics of groundwater sample.

Table 3.3: Characteristics of groundwater sample collected from a DTW pump station at BUET

Sl. No.	Parameter	Unit	Concentration
1	pH	--	6.6
2	Temperature	°C	28.1
3	Total Hardness	mg/l as $CaCO_3$	264
4	Total Alkalinity	mg/l as $CaCO_3$	218
5	Chloride (Cl^-)	mg/l	18.8
6	Electric Conductivity (EC)	µS/cm	710
7	Total Dissolved Solids (TDS)	mg/l	454.4
8	Phosphate (PO_4^{3-})	mg/l	0.54
9	Silica (SiO_2)	mg/l	66.0
10	Zinc (Zn^{2+})	mg/l	0.254
11	Calcium (Ca^{2+})	mg/l	72.2
12	Magnesium (Mg^{2+})	mg/l	19.3
13	Nickel (Ni^{2+})	mg/l	0.008
14	Copper (Cu^{2+})	mg/l	0.011

Since the estimated degree of supersaturation (Ω) of the natural groundwater was low, it was amended with Ca/ Carbonates/ NaOH to increase the Ω value (to facilitate precipitation of calcium carbonates). Batch experiments with amended natural groundwater were carried out under the following conditions:

(a) Amending the natural groundwater with sodium bi-carbonate solution (to increase concentration of carbonates) and increasing pH to above 8.0. Batch experiments were then carried out (as explained above), where Phosphate (at concentration of 1 and 4 mg/l) or Zn (at concentrations of 1 and 3 mg/l) were added to the amended groundwater and the precipitation of $CaCO_3$ was evaluated at different mixing times.

(b) Amending the natural groundwater with sodium bi-carbonate solution (to increase concentration of carbonates) and calcium chloride solution (to increase Ca concentration). Batch experiments were then carried out (as explained above), where Zn (at 0.25 and 1.0 mg/l) were added to the amended groundwater and the precipitation of $CaCO_3$ was evaluated at different mixing times.

(c) The pH of the natural groundwater was increased to about 8.0 through addition of dilute NaOH solution. Batch experiments were then carried out (as explained above), where Zn (at 0.25 and 1.0 mg/l) were added to the amended groundwater and the precipitation of $CaCO_3$ was evaluated at different mixing times.

MINEQL+ simulations were also carried out to understand the behavior of these experimental systems under “equilibrium” conditions.

3.3 Reagents and Analytical Methods

All chemicals used in this work were of reagent grade, and all stock solutions and standards were prepared with deionized water. Prior to use, all glassware was properly washed and rinsed with deionized water. Reagent grade $CaCl_2$ was used to prepare stock solution of calcium and reagent grade $NaHCO_3$ was used to prepare stock solutions of carbonate/bicarbonate. Phosphate stock solution was prepared using reagent grade potassium di-hydrogen phosphate; zinc stock solution was prepared using reagent grade $ZnCl_2$ solution.

A high precision electrical balance (Denver Instrument Company, AA–250) shown in**Error! Reference source not found.** was used for weighing. The pH and electrical conductivity were measured using a HQ 40d Multimeter, HACH. Calcium, Mg, Zn, Cu, and Ni concentrations were measured with an Atomic Absorption Spectrophotometer (Shimadzu, AA-6800). Hardness and alkalinity were measured with titrimetric method. Chloride was measured by Mohr’s method, Silica was measured by spectrophotometer according to standard method of American Water Works Association (AWWA) and phosphate was measured by spectrophotometer according to Molybdenum blue method.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

The overall objective of this research was to assess the effectiveness of Phosphate (PO_4^{3}) and Zinc (Zn^{2+}) as scale inhibitor in preventing or delaying the precipitation of Calcium Carbonate ($CaCO_3$). The detail methodology followed to carry out the research is presented in Chapter 3, including details of the batch experiments. This Chapter presents the results of the laboratory experiments carried out for assessing the scaling inhibition effect of zinc and phosphate in both NaCl electrolyte solution as well as in groundwater. It also presents results of MINEQL+ simulations of the experimental systems and analysis of the model outputs.

4.2 Effect of Phosphate on Precipitation of Calcium Carbonate in NaCl Solution

This Section presents the results of the laboratory experiments carried out (in 0.10 M NaCl solutions) to assess the inhibition effect of phosphate in delaying or preventing the precipitation of calcium carbonate.

4.2.1 Effect of Phosphate Concentration on Precipitation of $CaCO_3$

In order to assess the effect of phosphate inhibitor concentration on precipitation of $CaCO_3$, batch experiments were conducted in 0.10 M NaCl solutions, where calcium (Ca) concentration was fixed at 75 mg/l and phosphate concentration was varied from zero to 5 mg/l. Two sets of experiments were conducted, one for 30 minutes of mixing time and one for 5 hours of mixing time. Table 4.1(a) and 4.1(b) shows the experimental conditions and the experimental data from these two sets of experiments.

Table 4.1(a): Data from the batch experiments carried out to assess effect of phosphate concentration on precipitation of $CaCO_3$ (mixing time: 30 minutes)

Experimental Conditions:

Initial Ca^{2+} Concentration: 75 mg/L; Initial total Alkalinity: 200 mg/l as $CaCO_3$; Estimated HCO_3^-: 241 mg/l; Estimated CO_3^{2-}: 1.36 mg/l; Mixing time: 30 minutes; Estimated average super-saturation Index (Ω) = 11.87

Sample No.	pH	Temperature (°Celsius)	PO_4^{3-} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	8.04	24.9	0	64.8
2	8.08	24.7	0.1	66.4
3	8.08	24.6	0.25	67.2
4	8.02	24.5	0.5	68.8
5	8.07	25.0	0.75	70.4
6	8.09	24.8	1	71.2
7	8.11	24.5	2	72.0
8	8.27	24.5	3	72.8
9	7.89	24.8	4	73.6
10	7.94	24.7	5	75.0
Average	8.06	24.7	----	

Table 4.1(b): Data from the batch experiments carried out to assess effect of phosphate concentration on precipitation of $CaCO_3$ (mixing time: 5 hours)

Experimental Conditions:

Initial Ca^{2+} Concentration: 75 mg/L; Initial total Alkalinity: 200 mg/l as $CaCO_3$ Estimated HCO_3^-: 241 mg/l; Estimated CO_3^{2-}: 1.36 mg/l; Mixing time: 5 hours. Estimated average super-saturation Index (Ω) = 22.19

Sample No.	pH	Temperature (°Celsius)	PO_4^{3-} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	8.18	26.7	0	61.6
2	8.24	26.6	0.1	63.2
3	8.39	26.6	0.25	64.0
4	8.37	26.7	0.5	65.6
5	8.4	26.9	0.75	67.2
6	8.37	26.8	1	68.0
7	8.30	26.5	2	69.6
8	8.28	26.6	3	72.0
9	8.30	26.4	4	72.8
10	8.24	26.4	5	73.6
Average	8.31	26.6		

Figure 4.1(a) and 4.1(b) shows concentration of dissolved Ca and precipitated (calculated) Ca, respectively, as a function of phosphate concentration. Figure 4.1(a) shows that as phosphate concentration increases, dissolved Ca concentration in water increases; this was observed for two very different mixing times varying by a factor of 10. This means that as phosphate concentration increases, precipitation of Ca (as $CaCO_3$) decreases. Figure 4.1(a) shows that up to a phosphate concentration of about 1 mg/l, the dissolved Ca concentration increases rapidly with increase in phosphate concentration; then dissolved Ca concentration increases relatively slowly. The effect of phosphate in inhibiting $CaCO_3$ precipitation was more pronounced for a mixing time of 30 minutes; it appears that the inhibition effect of phosphate diminishes to some extent with time. The effect of mixing time has been discussed in more detail in Section 4.2.2.

Figure 4.1(b) shows calculated precipitated amount of Ca as a function of phosphate concentration. It shows that for a particular mixing time, concentration of precipitated Ca decreases as phosphate concentration increases. For example, for the batch experiment with 30 minutes of mixing time, amount of precipitated Ca^{2+} was 10.2 mg/l (or 14% of total Ca initially present in water) in the absence of any phosphate, while precipitated amount was almost zero at a phosphate concentration of 5 mg/l. For the batch experiment with 5-hour mixing time, amount of precipitated Ca was 13.4 mg/l (or 18% of total Ca initially present in water) in the absence of phosphate, while the precipitated amount was only 1.4 mg/l (or 2% of initial Ca) in the presence of 5 mg/l phosphate. Thus, it is clear that irrespective of mixing time, precipitation of Ca (as $CaCO_3$) decreases as phosphate concentration increases; the effect appears to be more pronounced for lower mixing time.

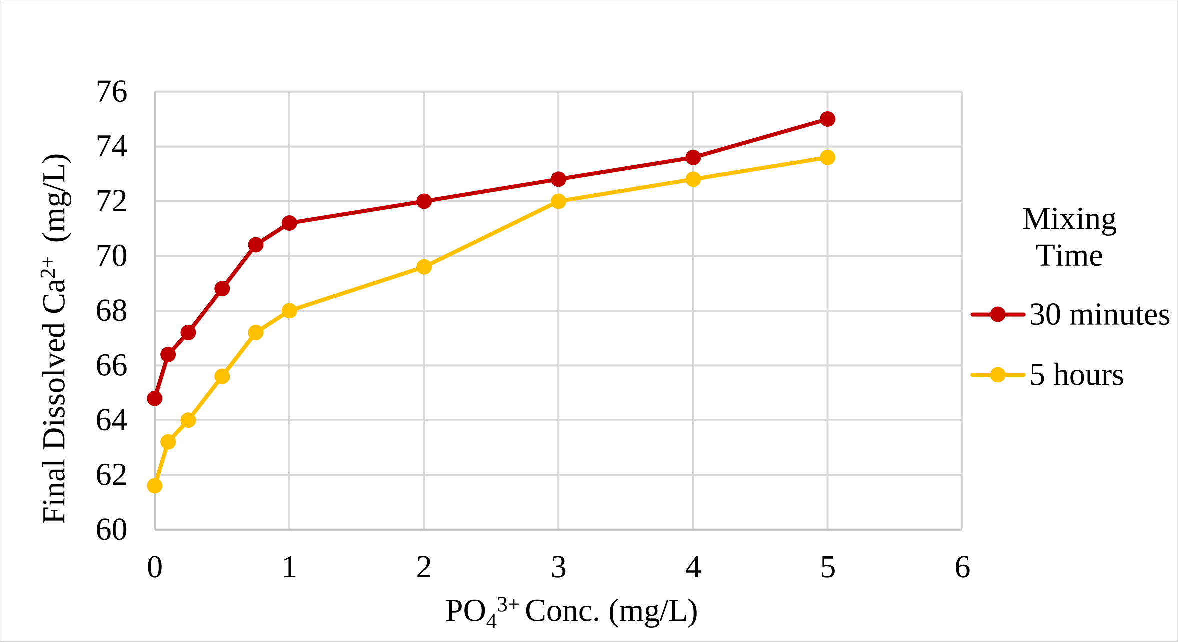


Figure 4.1(a): Concentration of dissolved Ca as a function of phosphate concentration (initial Ca = 75 mg/l)

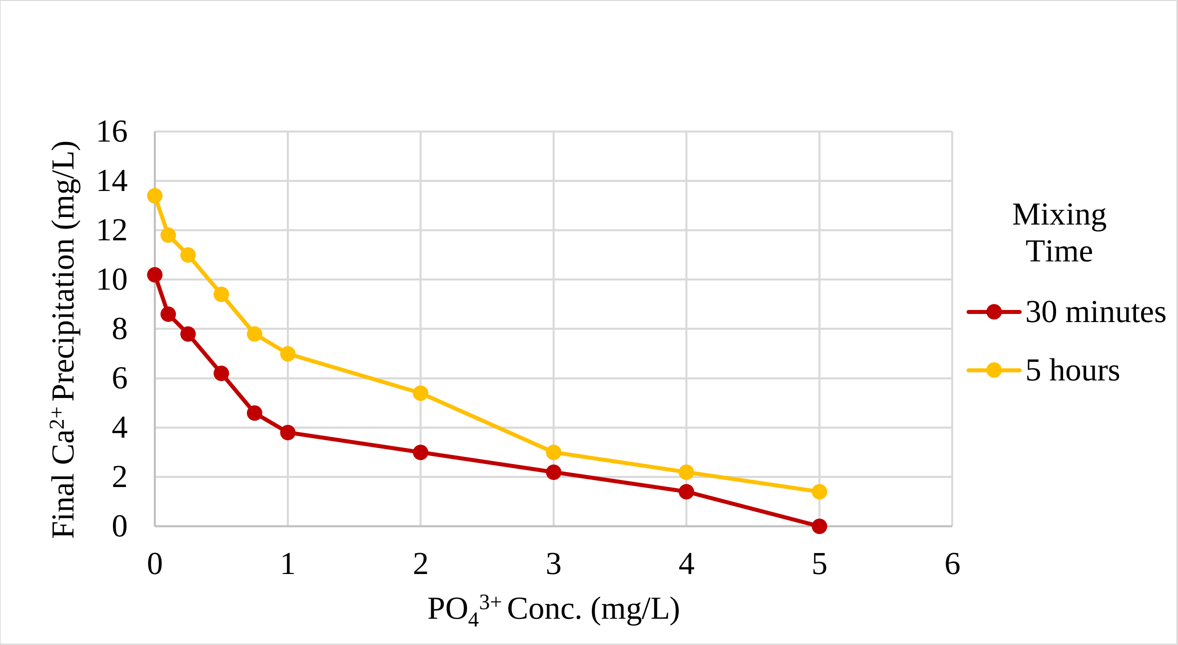


Figure 4.1(b): Concentration of precipitated Ca (calculated) as a function of phosphate concentration (initial Ca = 75 mg/l)

One interesting observation from Figs. 4.1(a) and 4.1(b) is that the effect of phosphate in inhibiting precipitation of $CaCO_3$ is more pronounced at lower phosphate concentrations. Fig. 4.1(b) shows that up to a phosphate concentration of about 1 mg/l, amount of precipitated Ca decreases rapidly as phosphate concentration increases; while at higher phosphate concentration it decreases at a lower rate. Figure 4.2(a) shows estimated slope of the line representing precipitated Ca versus phosphate concentration for phosphate concentration up to 1 mg/l; Fig. 4.2(b) shows estimated slope of the line representing precipitated Ca versus phosphate concentration for phosphate concentration from 1 to 5 mg/l.

The slopes of the lines represent the decrease of Ca precipitation for unit increase of phosphate inhibitor concentration. A steeper negative slope indicates faster decrease of Ca precipitation with increase in phosphate concentration and vice versa. Figure 4.2(a) shows a relatively steep negative slope (of about 6.2) for phosphate concentration up to 1 mg/l for both mixing times; while Fig. 4.2(b) shows a flatter negative slope (0.92 – 1.44) for phosphate concentration greater than 1 mg/l. Thus, effect of phosphate inhibitor concentration in inhibiting Ca precipitation is more pronounced at relatively lower concentrations of inhibitor.

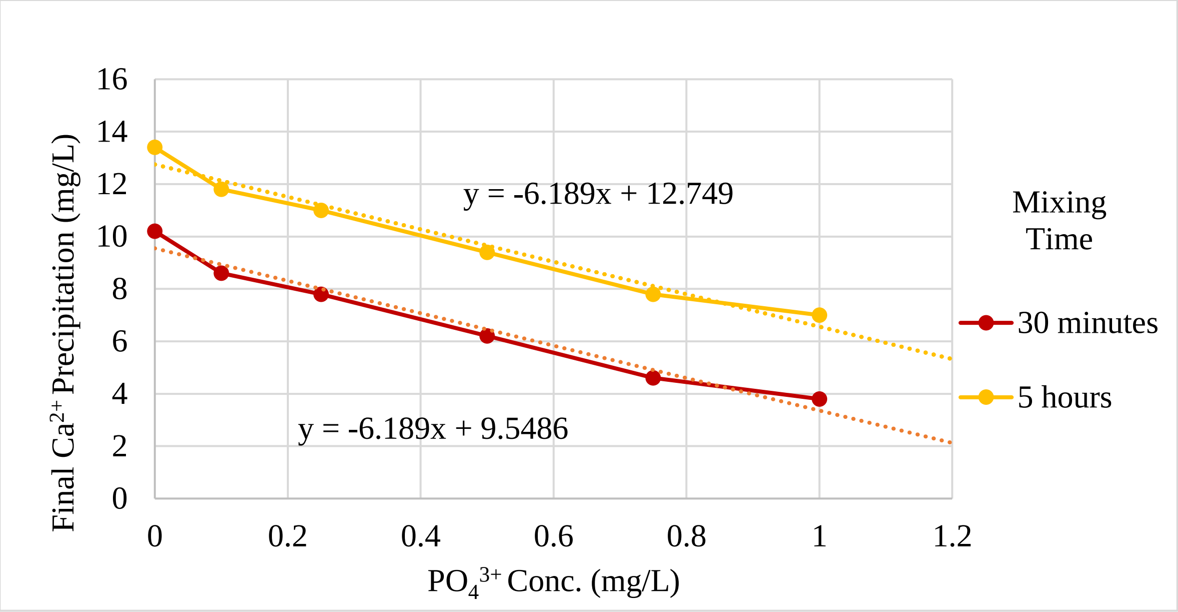


Figure 4.2(a): Concentration of precipitated Ca as a function of phosphate concentration for phosphate up to 1 mg/l; the dotted lines represent the best fit straight line through the experimental data.

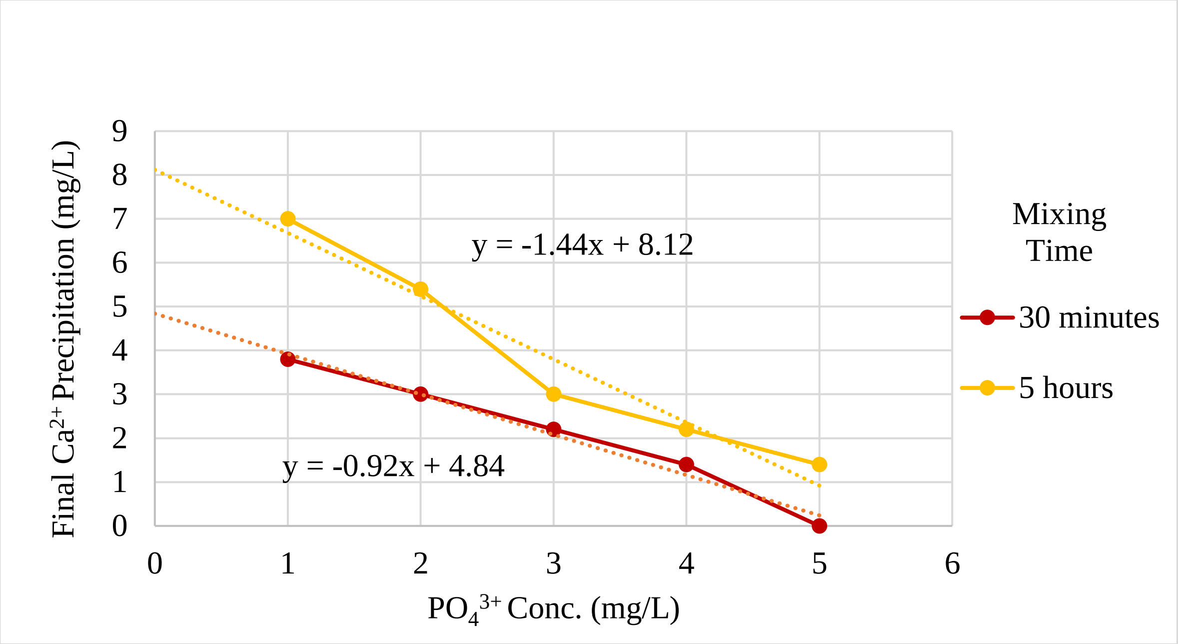


Figure 4.2(b): Concentration of precipitated Ca as a function of phosphate concentration for phosphate concentration 1 to 5 mg/l, the dotted lines represent the best fit straight line through the experimental data

4.2.2 Effect of Mixing Time

This Section presents the results of the batch experiments carried out to assess the effect of mixing time on precipitation of $CaCO_3$ in the presence of phosphate (as an inhibitor). Apart from the experiments with mixing time of 30 minutes and 5 hours (discussed above), two additional experiments were carried out with mixing times of 1 hour and 3 hours; both experiments were carried out in 0.10 M NaCl with initial Ca concentration of 75 mg/l. Table 4.2(a) and 4.2(b) shows the experimental conditions and the experimental data from these two sets of experiments. As noted above, in these experiments ten different phosphate inhibitor concentrations were used, varying from 0 to 5 mg/l.

Table 4.2(a): Data from the batch experiments carried out to assess effect of phosphate concentration on precipitation of $CaCO_3$ (mixing time: 1 hour)

Experimental Conditions: Initial Ca^{2+} Concentration: 75 mg/L; Initial total Alkalinity: 200 mg/l as $CaCO_3$ Estimated HCO_3^-: 241 mg/l; Estimated CO_3^{2-}: 1.36 mg/l; Mixing time: 1 hour; Average pH: ~8.3; Average Temperature: ~25 °Celsius		
Sample No.	PO_4^{3-} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	0	66.4
2	0.1	68
3	0.25	68.8
4	0.5	69.6
5	0.75	69.6
6	1	70.4
7	2	72.0
8	3	72.0
9	4	72.0
10	5	74.4

Table 4.2(b): Data from the batch experiments carried out to assess effect of phosphate concentration on precipitation of $CaCO_3$ (mixing time: 3 hours)

Experimental Conditions: Initial Ca^{2+} Concentration: 75 mg/L; Initial total Alkalinity: 200 mg/l as $CaCO_3$ Estimated HCO_3^-: 241 mg/l; Estimated CO_3^{2-}: 1.36 mg/l; Mixing time: 3 hours; Average pH: ~8.3; Average Temperature: ~25 °Celsius		
Sample No.	PO_4^{3-} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	0	62.4
2	0.1	64
3	0.25	66.4
4	0.5	67.2
5	0.75	68.0
6	1	68.8
7	2	68.8
8	3	69.6
9	4	71.2
10	5	75.0

Figures 4.3 (a, b, c, d, e, f, g, h, i, j) show variation of dissolved Ca concentration as a function of mixing time (0 hour to 5 hours) for all different phosphate concentrations used (up to 5 mg/l).

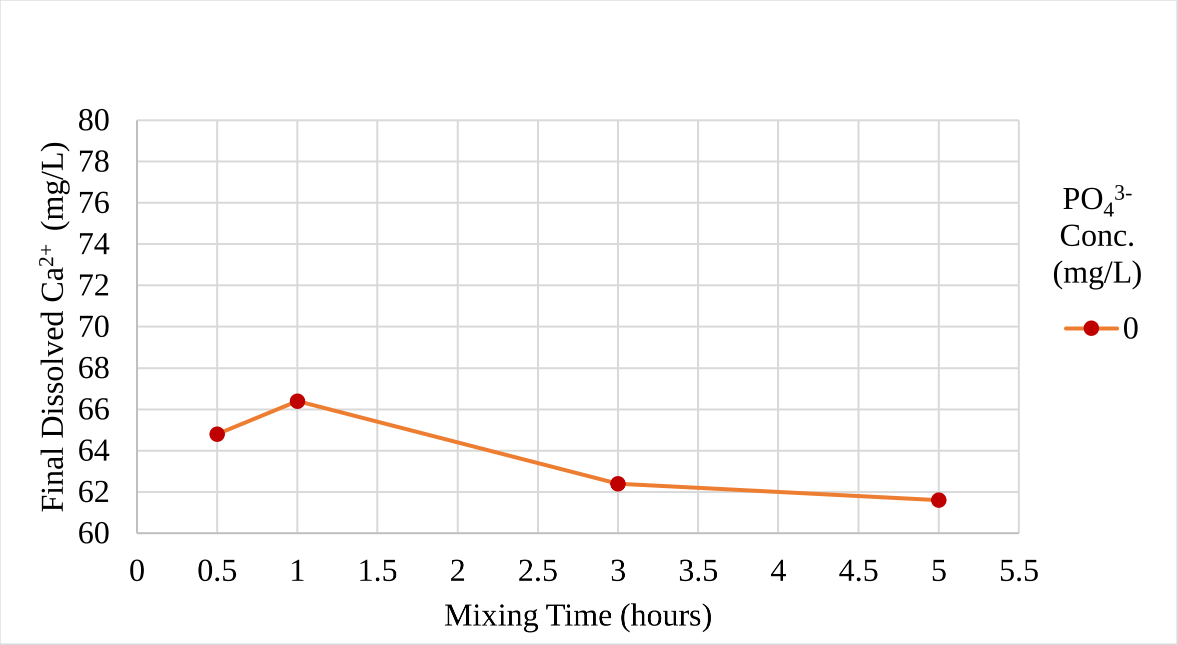


Figure 4.3(a): Final dissolved Ca^{2+} concentration with no PO_4^{3-} inhibitor

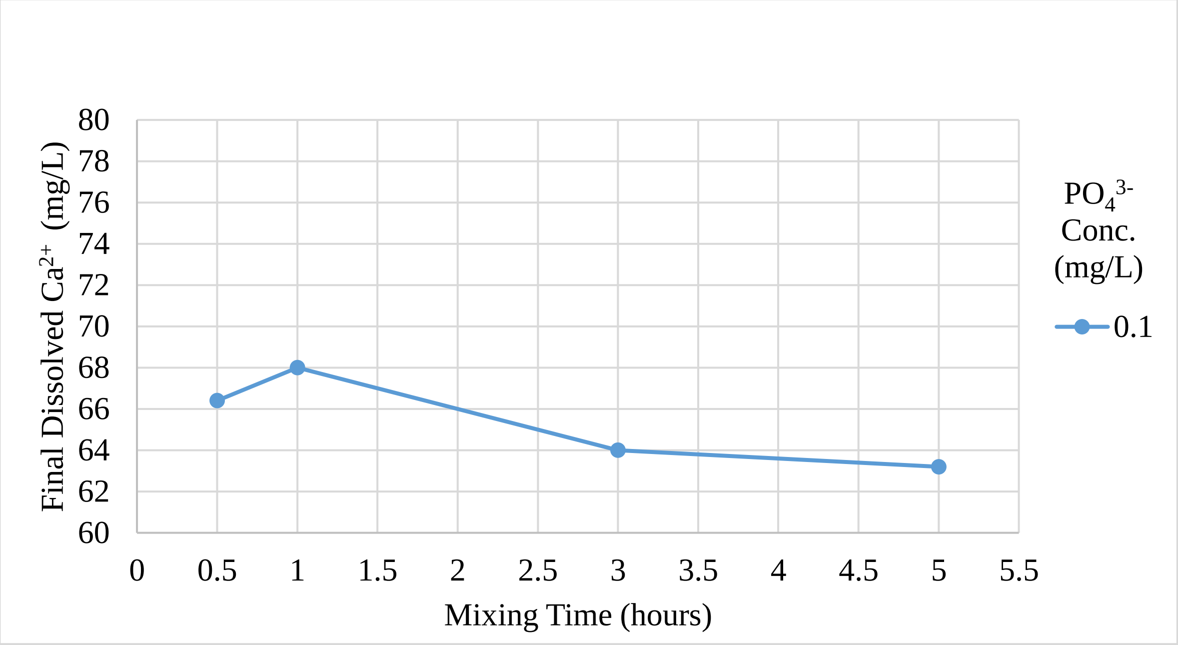


Figure 4.3(b): Final dissolved Ca^{2+} concentration with 0.1 mg/L PO_4^{3-} inhibitor

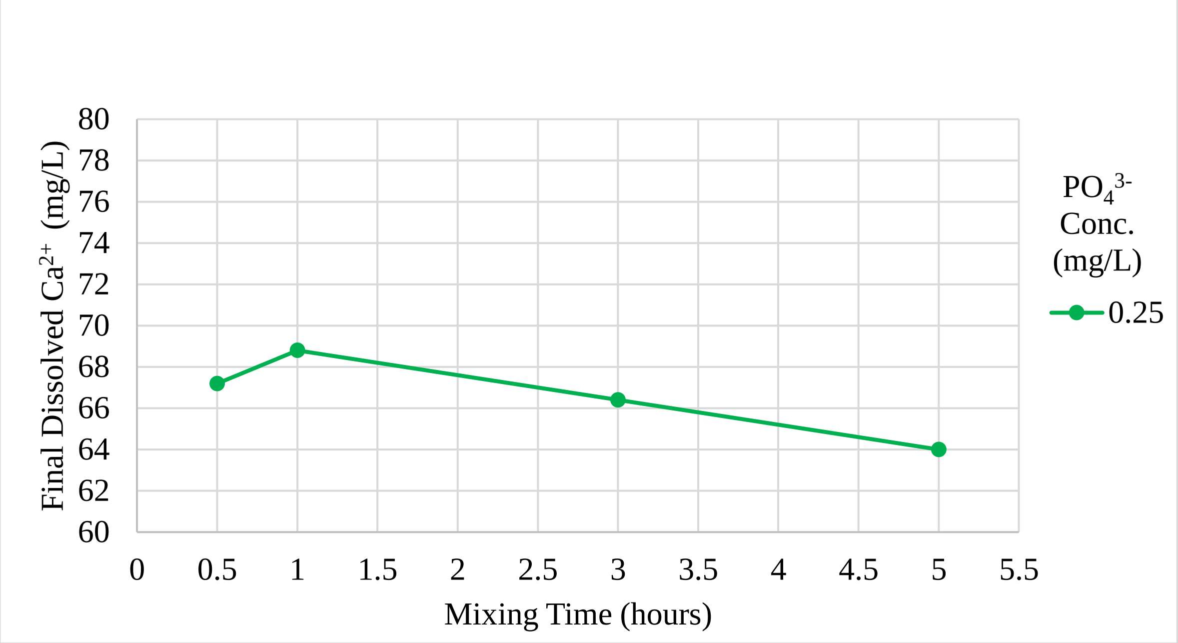


Figure 4.3(c): Final dissolved Ca^{2+} concentration with 0.25 mg/L PO_4^{3-} inhibitor

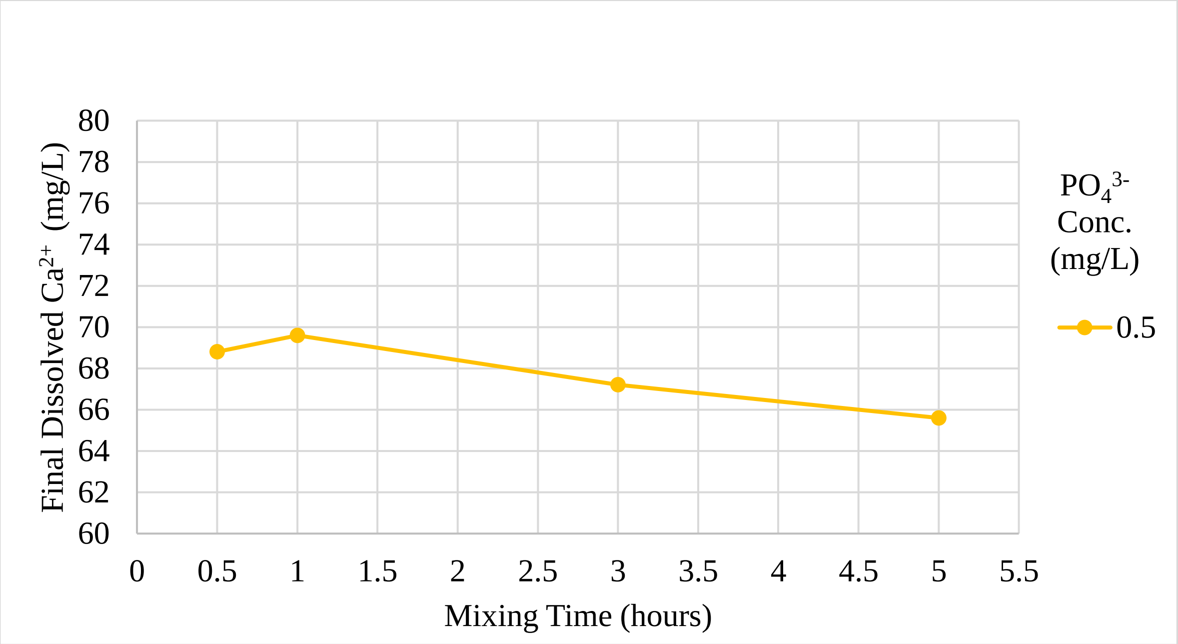


Figure 4.3(d): Final dissolved Ca^{2+} concentration with 0.5 mg/L PO_4^{3-} inhibitor

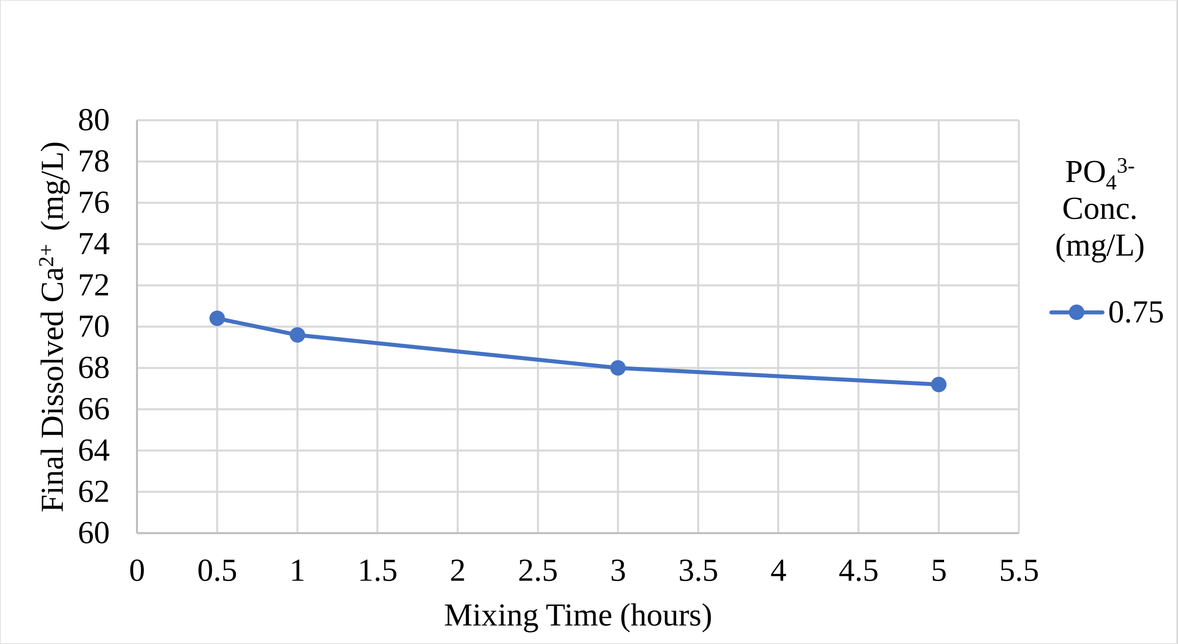


Figure 4.3(e): Final dissolved Ca^{2+} concentration with 0.75 mg/L PO_4^{3-} inhibitor

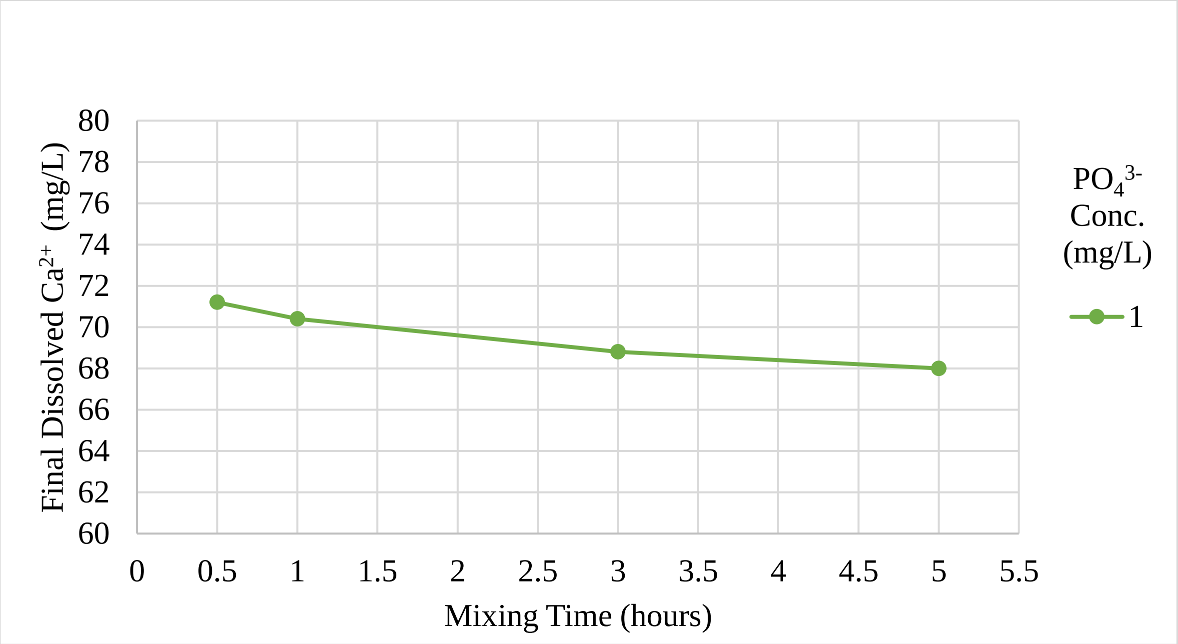


Figure 4.3(f): Final dissolved Ca^{2+} concentration with 1 mg/L PO_4^{3-} inhibitor

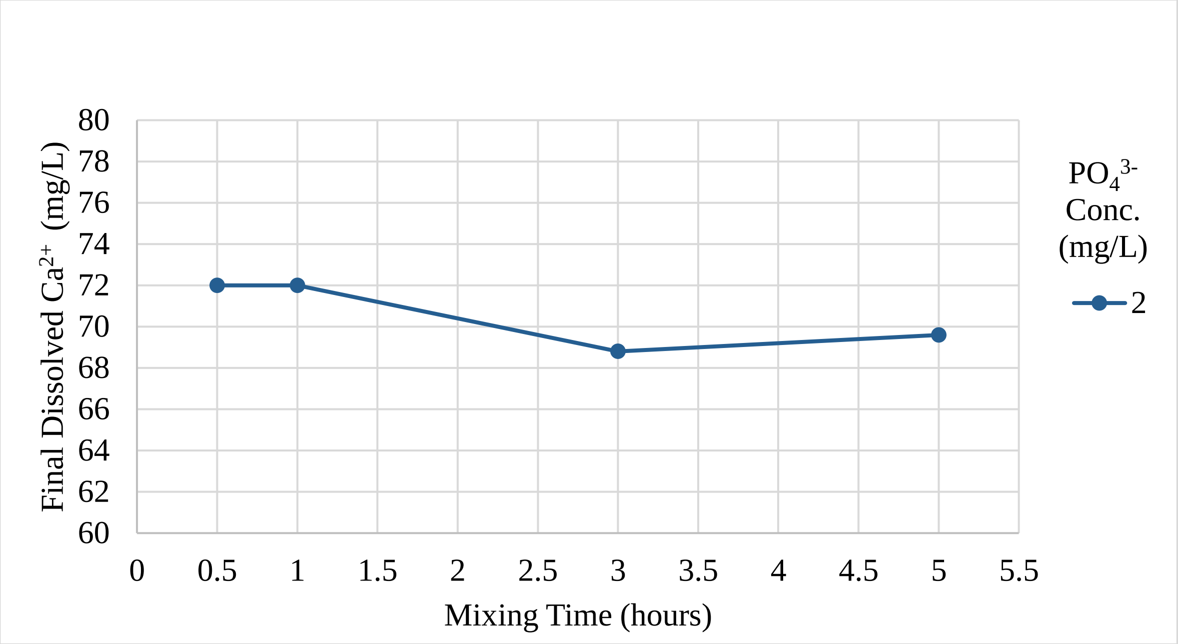


Figure 4.3(g): Final dissolved Ca^{2+} concentration with 2 mg/L PO_4^{3-} inhibitor

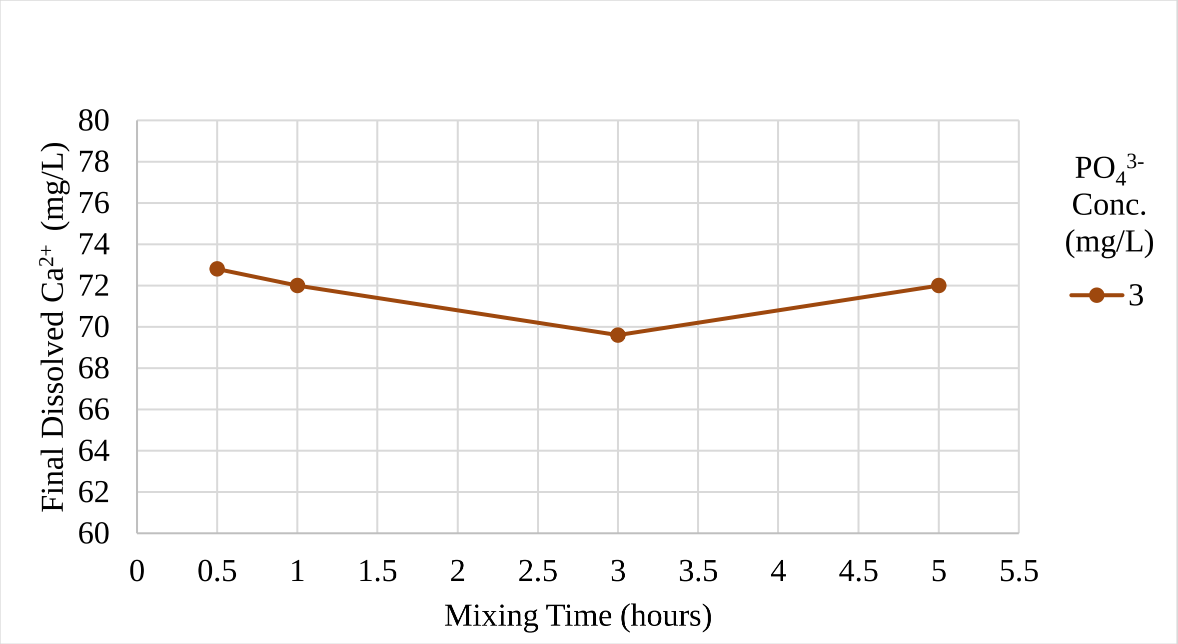


Figure 4.3(h): Final dissolved Ca^{2+} concentration with 3 mg/L PO_4^{3-} inhibitor

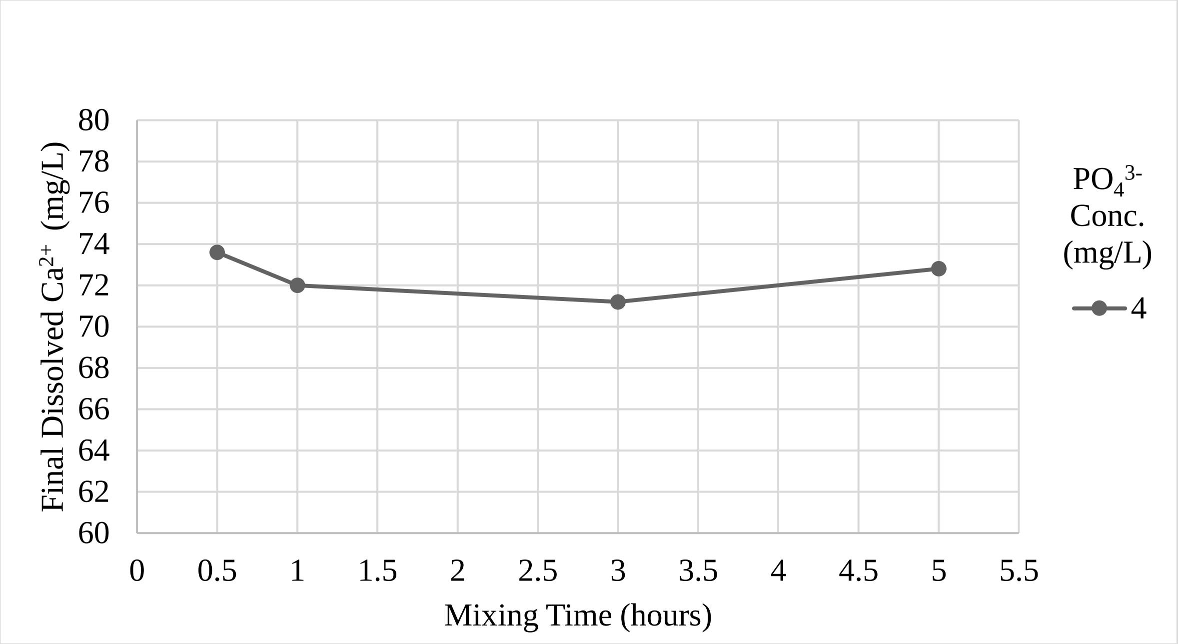


Figure 4.3(i): Final dissolved Ca^{2+} concentration with 4 mg/L PO_4^{3-} inhibitor

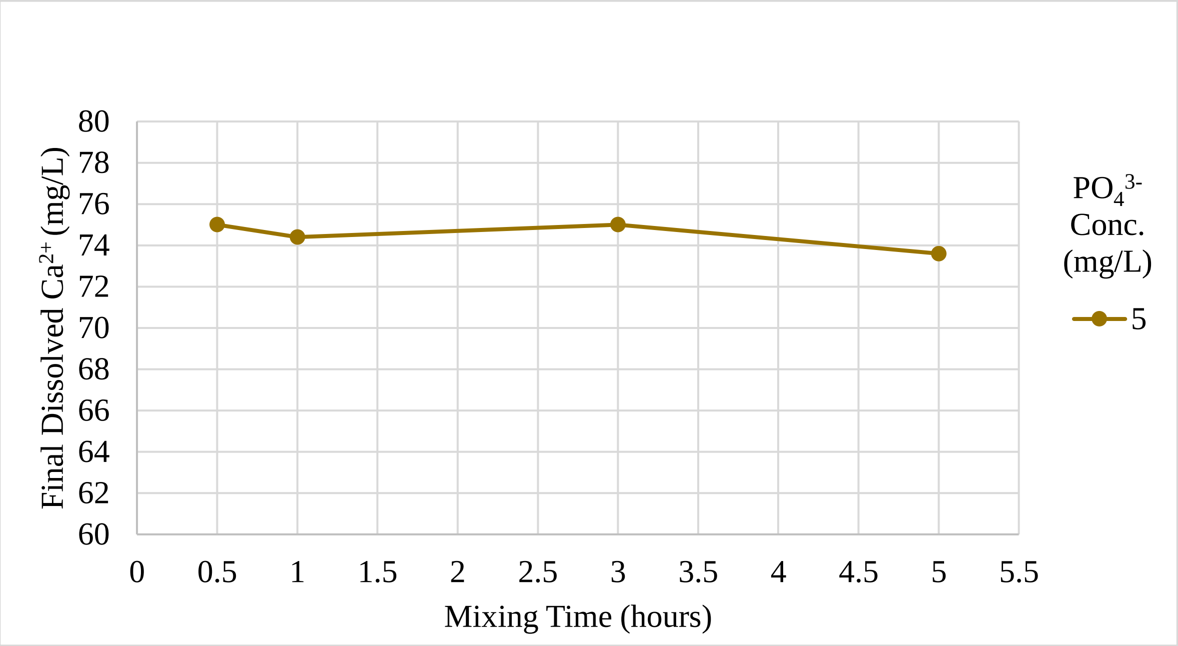


Figure 4.3(j): Final dissolved Ca^{2+} concentration with 5 mg/L PO_4^{3-} inhibitor

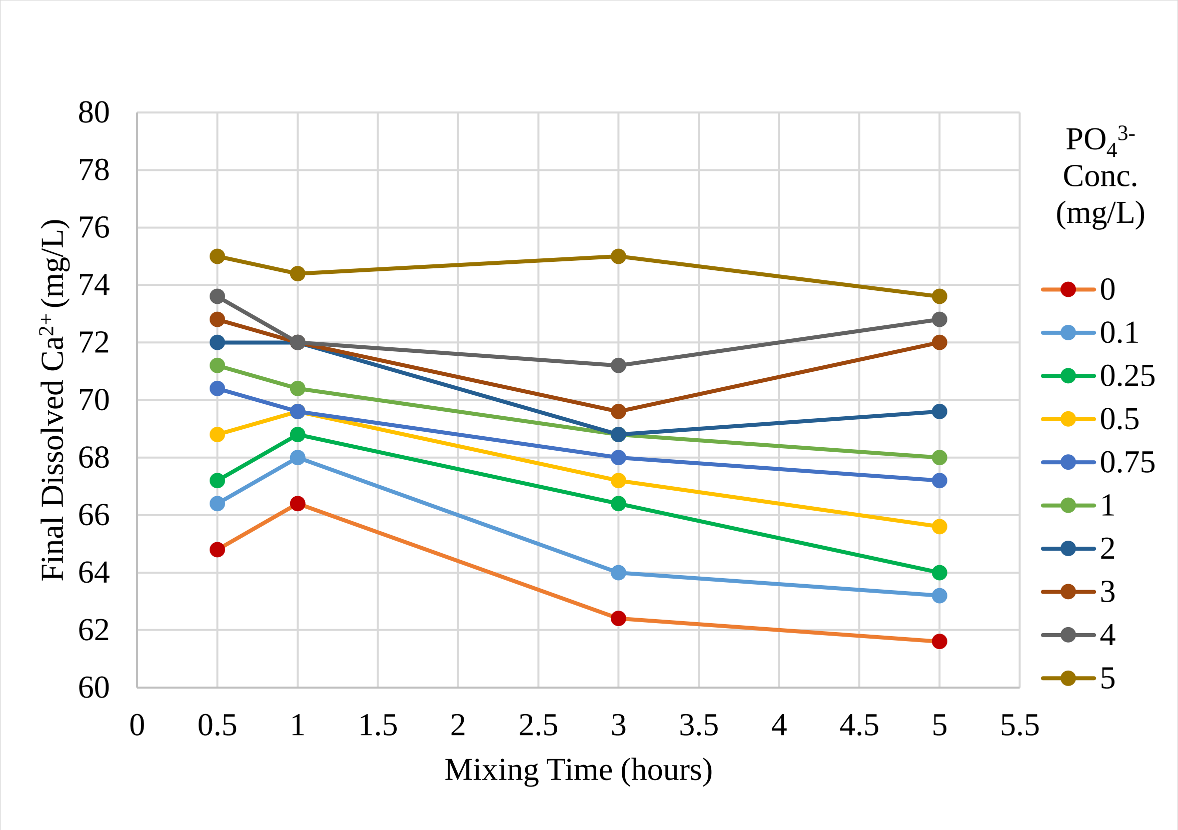


Figure 4.3(k): Final dissolved Ca^{2+} concentration with different concentrations of PO_4^{3-} inhibitor

From these figures (Fig. 4.3(a - j)), it can be concluded that for any particular condition, as time increases, the dissolved Ca^{2+} concentration decreases. That is with increasing time some precipitation takes place.

However, this trend appears to be slightly more pronounced for lower phosphate concentrations – up to about 1 mg/l. For example, for a phosphate concentration of 0.5 mg/l, dissolved Ca concentration was 68.8 mg/l at the end of 0.5 hr, but decreased to 65.6 mg/l at the end of 5 hours. Similarly, for a phosphate concentration of 0.75 mg/l, dissolved Ca concentration was 70.4 mg/l at the end of 0.5 hr, but decreased to 67.2 mg/l at the end of 5 hours. However, as phosphate concentration is increased beyond 1 mg/l, effect of time on Ca precipitation diminishes [Fig. 4.3 (a) through (j)]. For example, for a phosphate concentration of 4 mg/l, dissolved Ca concentration was 73.6 mg/l at the end of 0.5 hr, but decreases to 72.8 mg/l at the end of 5 hours.

4.2.3 Effect of Degree of Super-saturation (Ω)

Four sets of experiments were carried out to assess the effect of the degree of super-saturation on the precipitation of calcium carbonate. The experimental conditions of these four sets of experiments, in including calculated value of the degree of super-saturation, are summarized in Table 4.3. It shows that the degree of super-saturation in these four sets of experiments varied from 11.87 to 171.42. .

Table 4.3: Composition of solution in the batch experiments carried out to assess the effect of degree of saturation on $CaCO_3$ precipitation

Expt. No.	Average pH	Average Temp (°C)	Ca^{2+} (mg/l)	CO_3^{2-} (calculated) (mg/l)	Calculated Ω
1	8.06	24.70	75	1.36	11.87
2	8.31	22.86	100	2.41	26.49
3	8.16	25.31	150	1.71	30.40
4	8.80	25.67	200	7.13	171.42

Notes: (1) All experiments were carried out in 0.10 M NaCl solution;

(2) Mixing time in all experiments = 30 minutes

(3) Alkalinity in all experiments = 200 mg/L

(4) $K_{sp} = \text{antilog}\,[-171.9065 - 0.077993*T + \frac{2839.319}{T} + 71.595\log T]$

where T is temperature in Kelvin.

The experimental data for Expt. No. 1 in Table 4.3 are presented in Table 4.1(a); the experimental data for the remaining three experiments (Expt. Nos. 2, 3 and 4) are presented in Table 4.4(a-c).

Table 4.4(a): Data from the Batch Experiment No. 2 (as identified in Table 4.3) with initial Ca concentration of 100 mg/l

Sample No.	pH	Temperature (° C)	PO_4^{3-} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	8.41	22.8	0	86.4
2	8.38	22.8	0.1	88.0
3	8.45	22.8	0.25	88.8
4	8.43	22.7	0.5	89.6
5	8.34	22.6	0.75	90.4
6	8.27	22.7	1	93.6
7	8.26	22.8	2	95.2
8	8.24	22.9	3	96.8
9	8.2	23.0	4	98.4
10	8.15	23.5	5	99.2
Average	8.31	22.86		

Table 4.4(b): Data from the Batch Experiment No. 3 (as identified in Table 4.3) with initial Ca concentration of 150 mg/l

Sample No.	pH	Temperature (° Celsius)	PO_4^{3-} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	7.99	24.9	0	126.4
2	8.02	24.9	0.1	129.6
3	8.07	24.2	0.25	131.2
4	8.09	24.6	0.5	132.8
5	8.03	25.5	0.75	134.4
6	8.03	25.5	1	136.0
7	8.39	25.8	2	139.2
8	8.3	25.8	3	140.8
9	8.4	25.9	4	142.4
10	8.27	26.0	5	148.8
Average	8.16	25.3		

Table 4.4(c): Data from the Batch Experiment No. 4 (as identified in Table 4.3) with initial Ca concentration of 200 mg/l

Sample No.	pH	Temperature (° Celsius)	PO_4^{3-} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	8.8	25.6	0	168
2	8.8	25.6	0.1	171.2
3	8.8	25.6	0.25	172.8
4	8.8	25.7	0.5	174.4
5	8.8	25.7	0.75	179.2
6	8.8	25.7	1	180.0
7	8.8	25.7	2	180.8
8	8.8	25.7	3	184.0
9	8.8	25.7	4	184.0
10	8.8	25.7	5	185.6
Average	8.8	25.67		

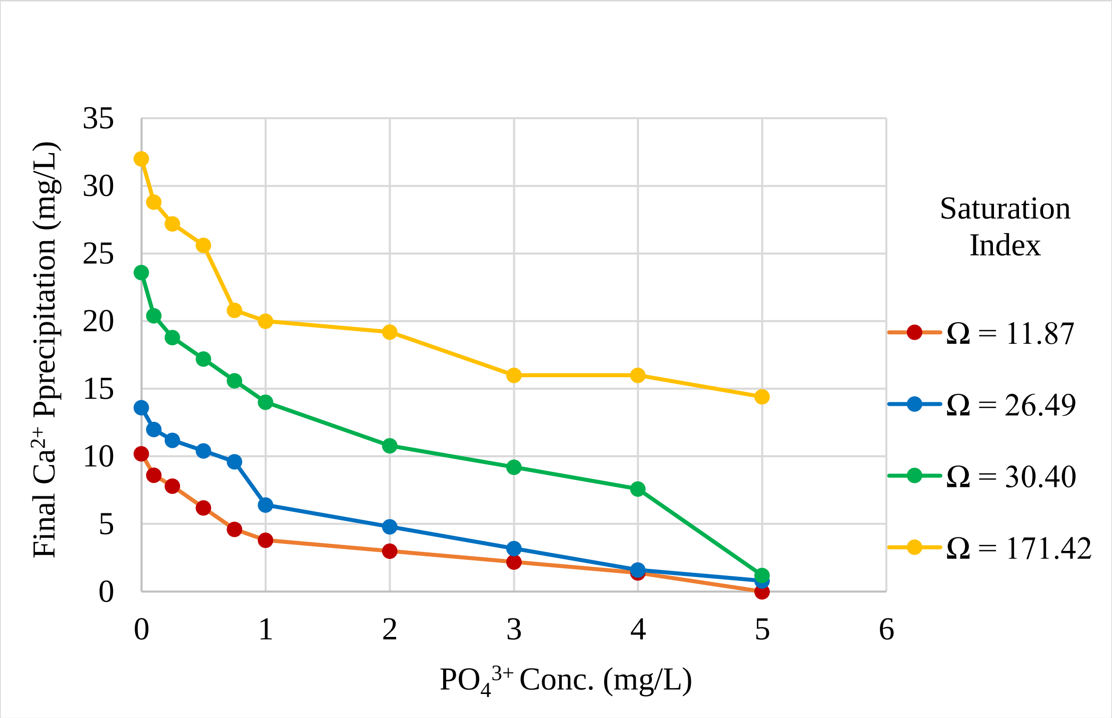


Figure 4.4: Concentration of precipitated Ca^{2+} as a function of phosphate concentration for four different degrees of super-saturation

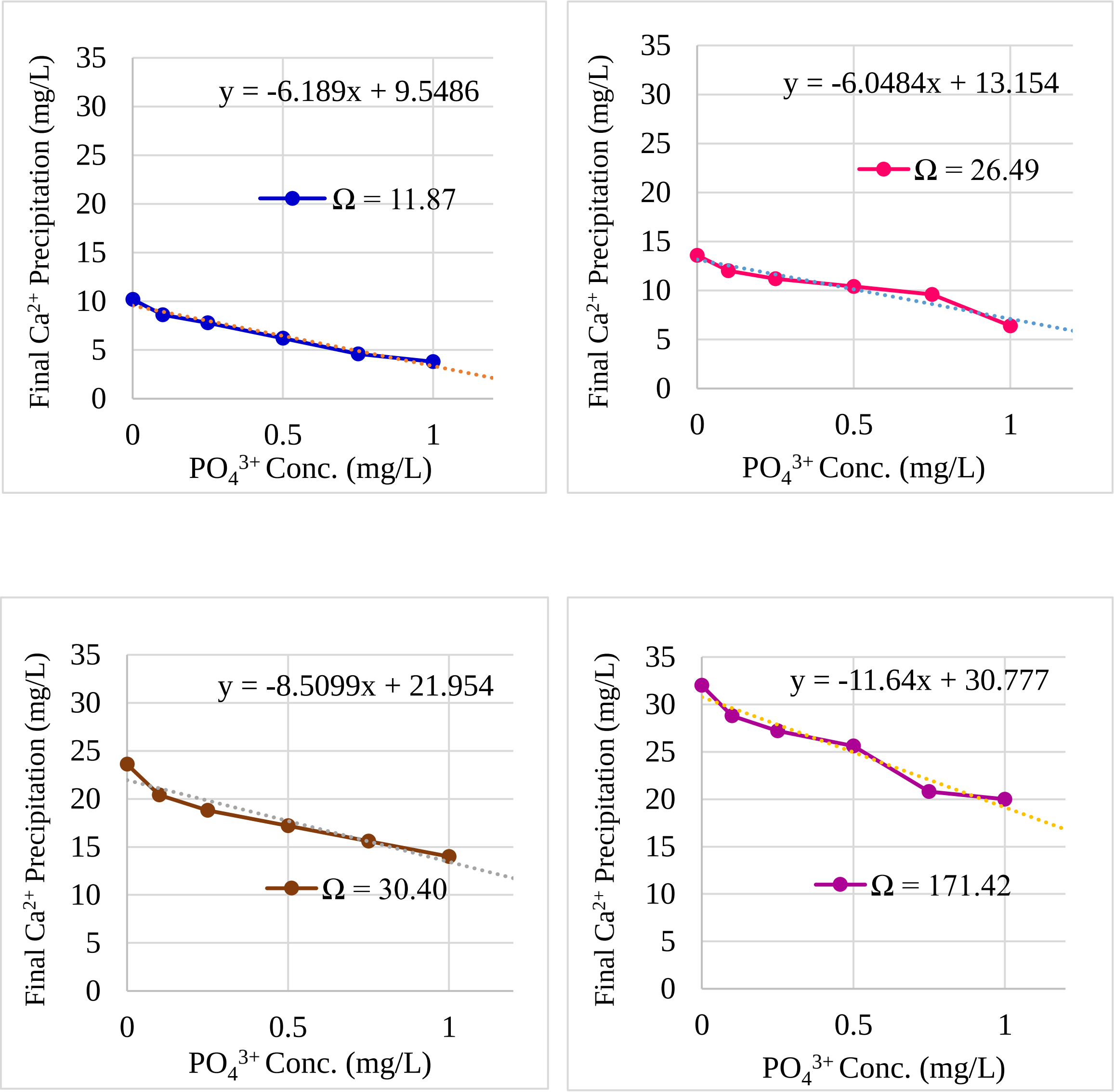


Figure 4.5(a): The slopes of the lines representing precipitated Ca concentration versus phosphate concentration for four different degrees of super-saturation (Ω) for phosphate concentration upto 1 mg/l

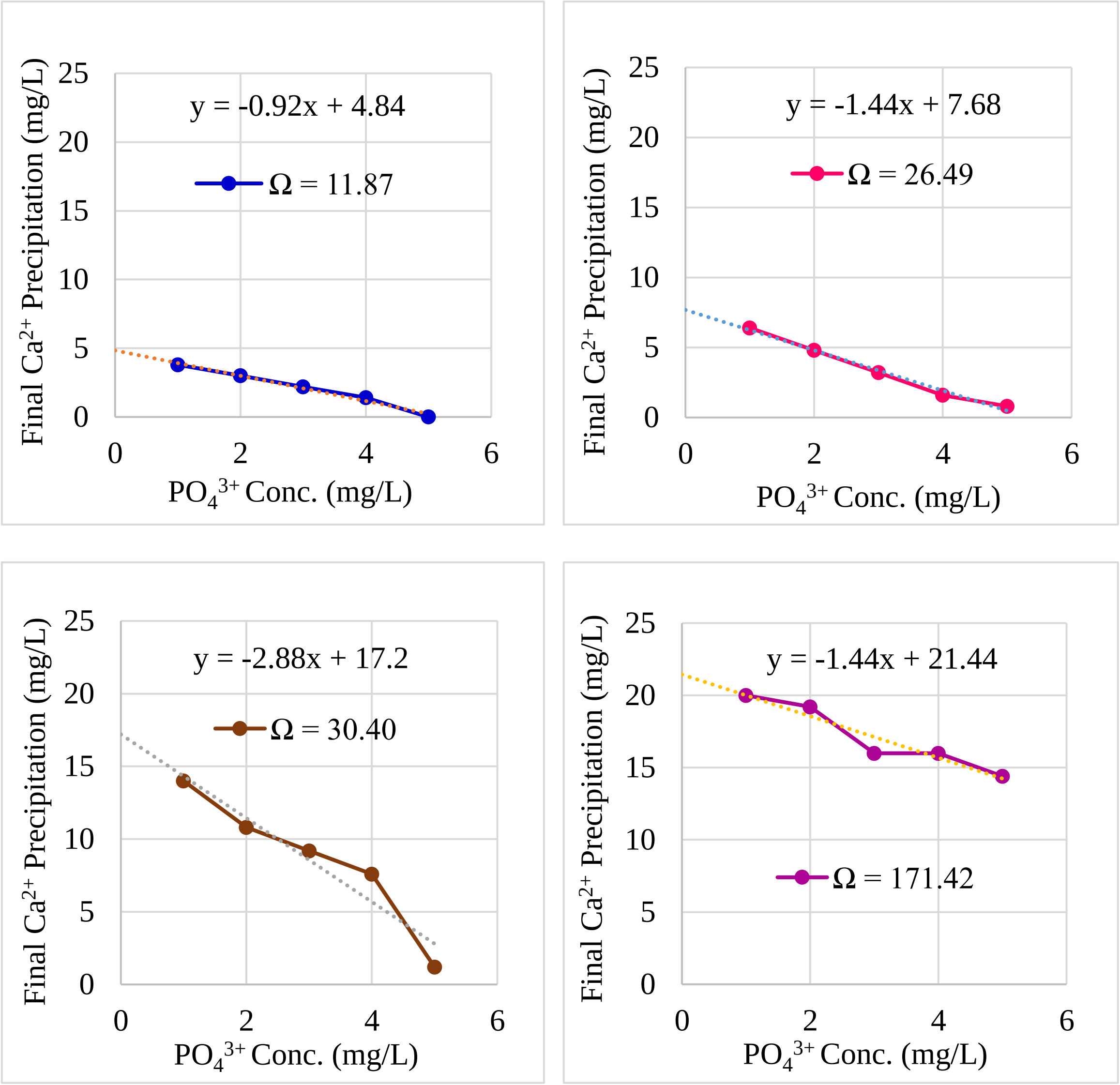


Figure 4.5(b): The slopes of the lines representing precipitated Ca concentration versus phosphate concentration for four different degrees of super-saturation (Ω) for phosphate concentration of 1 to 5 mg

Table 4.5 lists the slopes of the lines plotted in Fig. 4.5(a) and Fig. 4.5(b). It shows that for phosphate concentration up to 1 mg/l, the slope in general increased as the degree of super-saturation (Ω) increased. It means that precipitation of Ca would quickly decrease as we increase phosphate concentration; on the other hand, precipitation would quickly increase if phosphate concentration is decreased. However, the effect of the degree of super-saturation on precipitation is not so apparent at higher phosphate concentrations.

Table 4.5: Average slopes of lines for different ranges of phosphate concentration for different degrees of super-saturation

Expt. No.	Calculated Ω	Average Slope	
		Phosphate =0-1 mg/l	Phosphate =1-5 mg/l
1	11.87	-6.19	-0.92
2	26.49	-6.05	-1.44
3	30.40	-8.51	-2.88
4	171.4	-11.64	-1.44

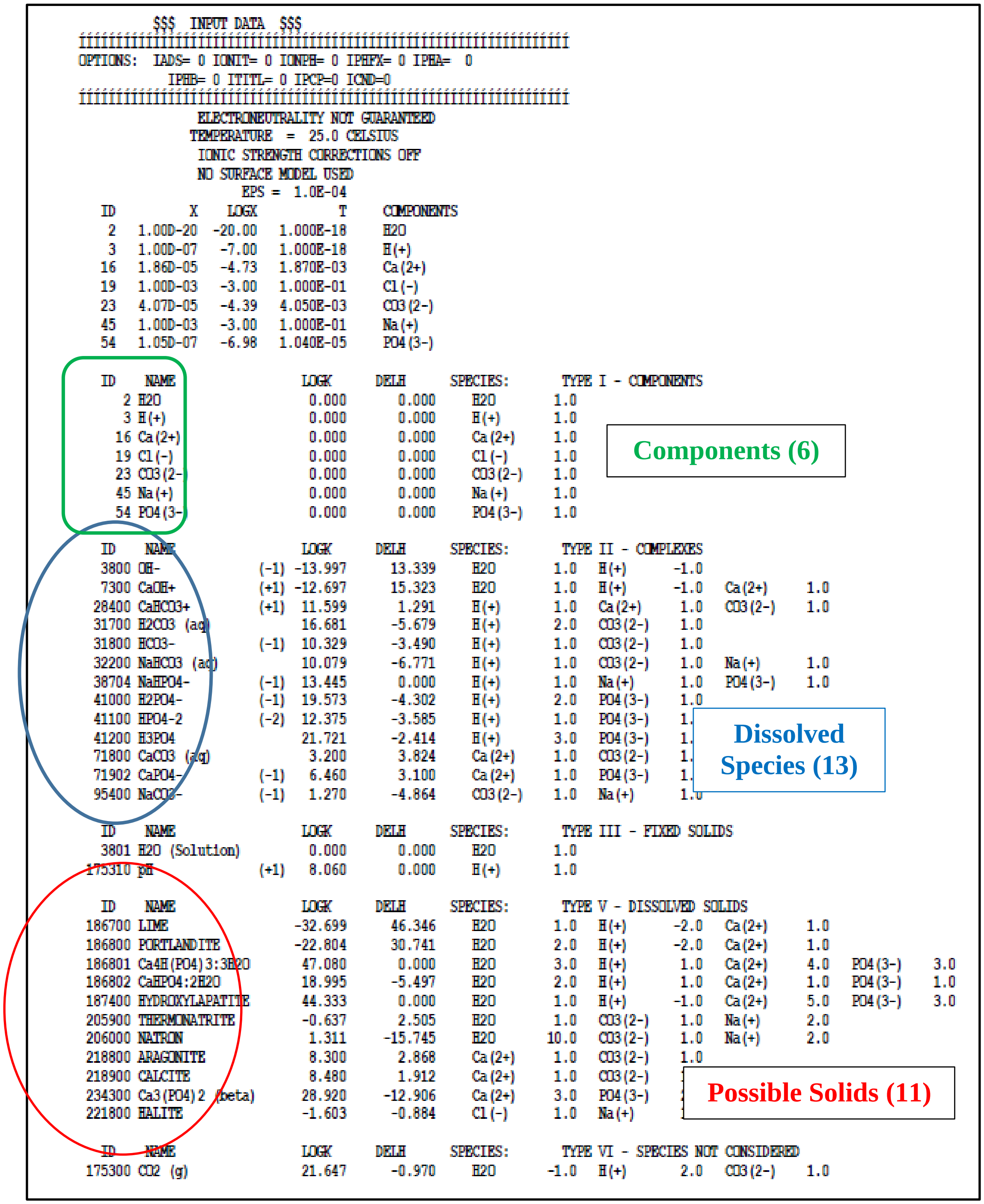
4.2.4 MINEQL+ Simulation of Experimental System with Phosphate

MINEQL+ simulations of the experimental systems were carried out to understand the precipitation of $CaCO_3$(s) under "equilibrium" condition, and how the experimental systems differ from the perfect "equilibrium" system. The following input ("recipe") was considered for the model simulation:

$(Ca)_T = 1.875 \times 10^{-3}$M (= 75 mg/l)
$(Na)_T = 0.10$ M
$(Cl^-)_T = 0.10$ M
pH = 8.06
Alkalinity = 4.0 meq/L (= 200 mg/l as $CaCO_3$) ("closed system" considered)
$(PO_4^{3-})_T = 0$ to 5.21×10^{-5} M (0 to 5 mg/l)

The MINEQL+ model input, dissolved species and solids considered (including equilibrium constants) are presented in the Table 4.6. It shows that the model considers 19 dissolved species (including 6 "components" selected for the simulations). The model also considers 11 solids that could possibly form as a result of reactions among the species present within the experimental systems. It should be noted that possible adsorption of phosphate on $CaCO_3$ crystals was considered in the simulation, because no such reaction has so far been confirmed, and therefore no such reactions are included in the MINEQL+ database.

Table 4.6: MINEQL+ model parameters (components, dissolved species, solids) for simulation of experimental systems in the presence of phosphate



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            $$$  INPUT DATA  $$$
ÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍ
OPTIONS:  IADS= 0 IONIT= 0 IONPH= 0 IPHFX= 0 IPHA=  0
               IPHB= 0 ITITL= 0 IPCP=0 ICND=0
ÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍÍ
                    ELECTRONEUTRALITY NOT GUARANTEED
                   TEMPERATURE  =  25.0 CELSIUS
                    IONIC STRENGTH CORRECTIONS OFF
                    NO SURFACE MODEL USED
                          EPS =  1.0E-04
   ID          X     LOGX           T     COMPONENTS
    2   1.00D-20  -20.00   1.000E-18     H2O
    3   1.00D-07   -7.00   1.000E-18     H(+)
   16   1.86D-05   -4.73   1.870E-03     Ca(2+)
   19   1.00D-03   -3.00   1.000E-01     Cl(-)
   23   4.07D-05   -4.39   4.050E-03     CO3(2-)
   45   1.00D-03   -3.00   1.000E-01     Na(+)
   54   1.05D-07   -6.98   1.040E-05     PO4(3-)

   ID    NAME                 LOGK      DELH      SPECIES:      TYPE I - COMPONENTS
      2 H2O                   0.000      0.000     H2O          1.0
      3 H(+)                  0.000      0.000     H(+)         1.0
     16 Ca(2+)                0.000      0.000     Ca(2+)       1.0
     19 Cl(-)                 0.000      0.000     Cl(-)        1.0
     23 CO3(2-)               0.000      0.000     CO3(2-)      1.0
     45 Na(+)                 0.000      0.000     Na(+)        1.0
     54 PO4(3-)               0.000      0.000     PO4(3-)      1.0

   ID    NAME                 LOGK      DELH      SPECIES:      TYPE II - COMPLEXES
   3800 OH-            (-1) -13.997     13.339     H2O          1.0   H(+)       -1.0
   7300 CaOH+          (+1) -12.697     15.323     H2O          1.0   H(+)       -1.0    Ca(2+)      1.0
  28400 CaHCO3+        (+1)  11.599      1.291     H(+)         1.0   Ca(2+)      1.0    CO3(2-)     1.0
  31700 H2CO3 (aq)           16.681     -5.679     H(+)         2.0   CO3(2-)     1.0
  31800 HCO3-          (-1)  10.329     -3.490     H(+)         1.0   CO3(2-)     1.0
  32200 NaHCO3 (aq)          10.079     -6.771     H(+)         1.0   CO3(2-)     1.0    Na(+)       1.0
  38704 NaHPO4-        (-1)  13.445      0.000     H(+)         1.0   Na(+)       1.0    PO4(3-)     1.0
  41000 H2PO4-         (-1)  19.573     -4.302     H(+)         2.0   PO4(3-)     1.0
  41100 HPO4-2         (-2)  12.375     -3.585     H(+)         1.0   PO4(3-)     1.
  41200 H3PO4                21.721     -2.414     H(+)         3.0   PO4(3-)     1.
  71800 CaCO3 (aq)            3.200      3.824     Ca(2+)       1.0   CO3(2-)     1.
  71902 CaPO4-         (-1)   6.460      3.100     Ca(2+)       1.0   PO4(3-)     1.
  95400 NaCO3-         (-1)   1.270     -4.864     CO3(2-)      1.0   Na(+)       1.0

   ID    NAME                 LOGK      DELH      SPECIES:      TYPE III - FIXED SOLIDS
   3801 H2O (Solution)        0.000      0.000     H2O          1.0
 175310 pH             (+1)   8.060      0.000     H(+)         1.0

   ID    NAME                 LOGK      DELH      SPECIES:      TYPE V - DISSOLVED SOLIDS
 186700 LIME                -32.699     46.346     H2O          1.0   H(+)       -2.0    Ca(2+)      1.0
 186800 PORTLANDITE         -22.804     30.741     H2O          2.0   H(+)       -2.0    Ca(2+)      1.0
 186801 Ca4H(PO4)3:3H2O      47.080      0.000     H2O          3.0   H(+)        1.0    Ca(2+)      4.0   PO4(3-)     3.0
 186802 CaHPO4:2H2O          18.995     -5.497     H2O          2.0   H(+)        1.0    Ca(2+)      1.0   PO4(3-)     1.0
 187400 HYDROXYLAPATITE      44.333      0.000     H2O          1.0   H(+)       -1.0    Ca(2+)      5.0   PO4(3-)     3.0
 205900 THERMONATRITE        -0.637      2.505     H2O          1.0   CO3(2-)     1.0    Na(+)       2.0
 206000 NATRON                1.311    -15.745     H2O         10.0   CO3(2-)     1.0    Na(+)       2.0
 218800 ARAGONITE             8.300      2.868     Ca(2+)       1.0   CO3(2-)     1.0
 218900 CALCITE               8.480      1.912     Ca(2+)       1.0   CO3(2-)     1
 234300 Ca3(PO4)2 (beta)     28.920    -12.906     Ca(2+)       3.0   PO4(3-)     2
 221800 HALITE               -1.603     -0.884     Cl(-)        1.0   Na(+)       1

   ID    NAME                 LOGK      DELH      SPECIES:      TYPE VI - SPECIES NOT CONSIDERED
 175300 CO2 (g)              21.647     -0.970     H2O         -1.0   H(+)        2.0    CO3(2-)     1.0
```

The model outputs show that under "equilibrium condition", over 86% of Ca precipitates as $CaCO_3$(s) (for all phosphate concentrations), and phosphate has virtually no effect on precipitation of Ca. Predicted dissolved Calcium (Ca^{2+}) concentration was 10.96 mg/l for no phosphate, and 10.6 mg/l for the highest phosphate concentration of 5 mg/l (5.21 x 10^{-5} M). On the other hand, in the batch experiments, dissolved Ca concentration was over 60 mg/l in the absence of phosphate, and it increased further in the presence of phosphate. Thus, a comparison of MINEQL+ simulations and the experimental results clearly show that the formation/precipitation of $CaCO_3$(s) is limited by the (slow) kinetics of calcium carbonate formation.

Figure 4.6 shows distribution of Ca species for the simulation with phosphate concentration of 1.0 mg/l (1.04 x 10^{-5} M). It shows that Ca^{2+} is the dominant dissolved Ca species, with a concentration of 10.88 mg/l (or 2.72 x 10^{-3} M). On the other hand, Calcite [$CaCO_3$(s)] is the dominant precipitated form of Ca, with a concentration of 62.4 mg/l (or 1.56 x 10^{-3} M). The slight decrease in dissolved Ca concentration with increasing phosphate concentration is due to the formation of the solid Hydroxyapatite [$Ca_5(PO_4)_3(OH)$(s)] at higher phosphate concentration (as discussed below).

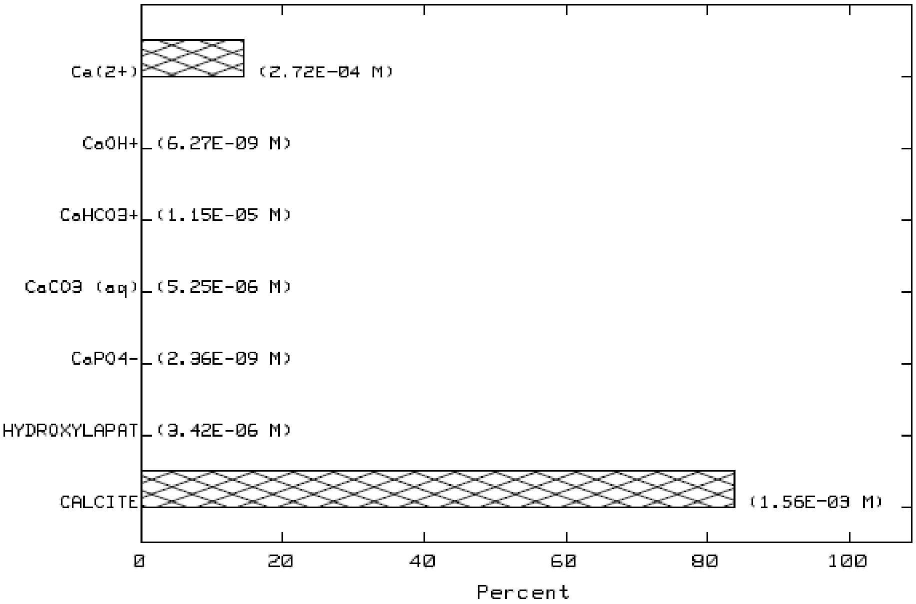


Figure 4.6: Distribution of Ca species in the experimental system with a phosphate concentration of 1.0 mg/l (1.04 x 10^{-5} M)

Speciation of Phosphate Species in Water and its Possible Effects:

One interesting observation from the model simulations was the distribution of phosphate species in the experimental systems under "equilibrium" condition. According to the model outputs, almost the entire phosphate added to the system would precipitate as Hydroxyapatite [$Ca_5(PO_4)_3(OH)(s)$] under "equilibrium" condition. Figure 4.7 shows distribution of phosphate species (MINEQL+) for the simulation with phosphate concentration of 1.0 mg/l (1.04 x 10^{-5} M); it shows that almost the entire phosphate is present as Hydroxyapatite.

This suggest that under "favorable" conditions (e.g., longer equilibration time), phosphate would tend to precipitate as Hydroxyapatite in the experimental systems. However, since dissolved phosphate (orthophosphate) was detected and measured in the experimental systems, it appears that formation of Hydroxyapatite is limited by the slow kinetics of its formation and is unlikely to form the experimental systems.

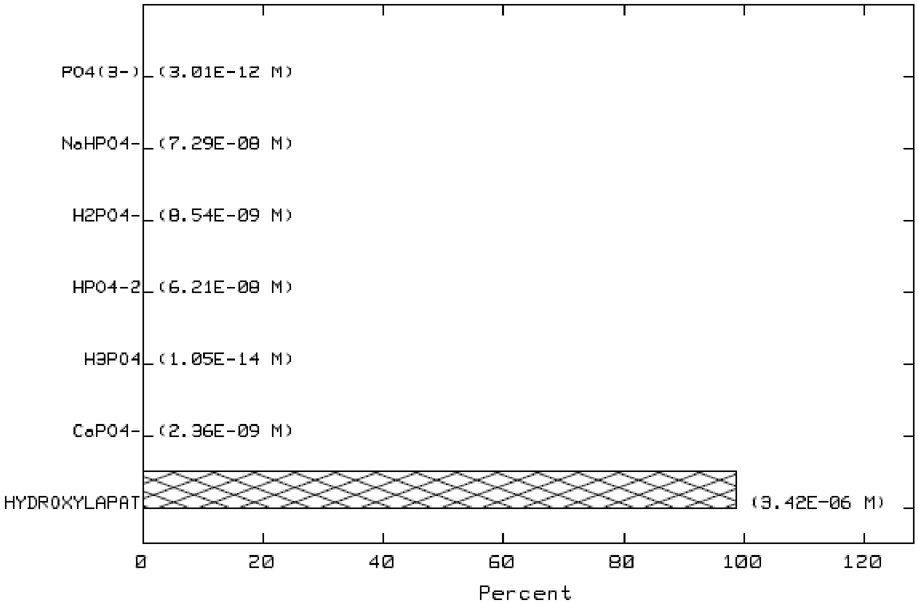


Figure 4.7: Distribution of phosphate species in the experimental system with a phosphate concentration of 1.0 mg/l (1.04 x 10^{-5} M), showing that almost the entire phosphate is present in Hydroxyapatite

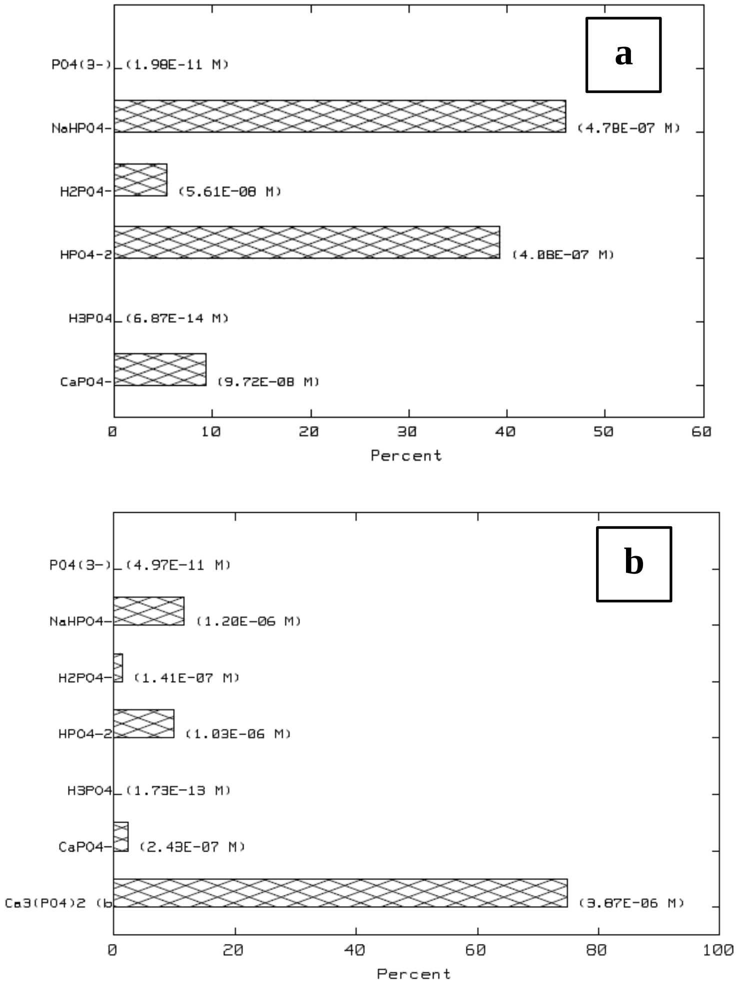
As discussed earlier, the inhibition mechanism of phosphate is reported to be the adsorption of orthophosphate on the $CaCO_3$ crystals and the resulting slowing down of crystal growth. In order to evaluate the speciation of phosphate in the experimental systems, additional MINEQL+ simulations were carried out, where formation or precipitation of Hydroxyapatite was intentionally suppressed. In addition, precipitation of calcium carbonate (both calcite and apatite) was also suppressed.

Table 4.7: Results of MINEQL+ simulations, where formation/precipitation of calcium carbonate and Hydroxyapatite was suppressed [Model system: $(Ca)_T = 1.875 \times 10^{-3}$ M (= 75 mg/l); $(Na)_T = 0.10$ M; $(Cl^-)_T = 0.10$ M; pH = 8.06; Alkalinity = 4.0×10^{-3} eq/L (= 200 mg/l as $CaCO_3$)]

Model Run No.	Total Phosphate	Ca^{2+} [M]	Orthophosphate [M]
1	0 M (0 mg/l)	1.71×10^{-3}	--
2	1.04×10^{-6} M (0.10 mg/l)	1.71×10^{-3}	4.64×10^{-7}
3	2.60×10^{-6} M (0.25 mg/l)	1.70×10^{-3}	1.16×10^{-6}
4	5.21×10^{-6} M (0.50 mg/l)	1.70×10^{-3}	1.16×10^{-6}
5	7.81×10^{-6} M (0.75 mg/l)	1.70×10^{-3}	1.16×10^{-6}
6	1.04×10^{-5} M (1.0 mg/l)	1.69×10^{-3}	1.17×10^{-6}
7	2.08×10^{-5} M (2.0 mg/l)	1.68×10^{-3}	1.18×10^{-6}
8	3.125×10^{-5} M (3.0 mg/l)	1.67×10^{-3}	1.195×10^{-6}
9	4.167×10^{-5} M (4.0 mg/l)	1.65×10^{-3}	1.217×10^{-6}
10	5.121×10^{-5} M (5.0 mg/l)	1.64×10^{-3}	1.22×10^{-6}

Table 4.7 shows the results of model simulations of the experimental system, where formation/precipitation of calcium carbonate and Hydroxyapatite was suppressed. It shows that (in the absence of the precipitation of calcium carbonate), Ca^{2+} is the dominant Ca species in the system; the slight decrease in Ca^{2+} concentration at higher phosphate concentration is due to the precipitation of a portion of Ca as the solid $Ca_3(PO_4)_2(s)$. The last

column of Table 4.7 shows the simulated concentrations of orthophosphate [∑ (H_3PO_4 + $H_2PO_4^-$ + HPO_4^{2-} + PO_4^{3-})] in the experimental systems. It shows that orthophosphate concentration initially increases with increasing concentration of phosphate (up to a phosphate concentration of about 0.5 mg/l); however, as phosphate concentration increases further, $Ca_3(PO_4)_2$(s) begins to form, which limits the increase of orthophosphate concentration. Figure 4.8 shows speciation of phosphate at three different phosphate concentrations, showing that $Ca_3(PO_4)_2$(s) becomes the dominant phosphate species at higher (greater than about 1.0 mg/l) phosphate concentrations. It shows that at a phosphate concentration of 0.10 mg/l, $NaHPO_4^-$ and HPO_4^{2-} are dominant species; however, at phosphate concentrations of 1.0 mg/l and 5.0 mg/l, $Ca_3(PO_4)_2$(s) becomes the dominant species accounting for majority of phosphate in the system.



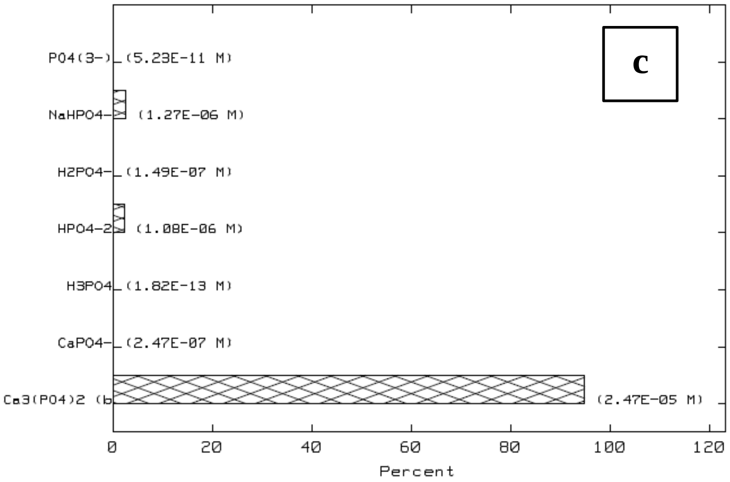


Figure 4.8: MINEQL+ outputs showing distribution of phosphate species in the experimental systems for: (a) phosphate = 0.10 mg/l (1.04 x 10^{-6} M); (b) phosphate = 1.0 mg/l (1.04 x 10^{-5} M); (c) phosphate 5.0 mg/l (5.21 x 10^{-5} M)

Thus, the model simulations suggest that, in the presence of Calcium, phosphate would tend to precipitate Ca-PO_4 solids [e.g., Hydroxyapatite and/or $Ca_3(PO_4)_2(s)$] under favorable conditions, especially at higher phosphate concentrations. So, concentration of orthophosphate (which is apparently responsible for the inhibition effect of phosphate) would not increase proportionately to the total concentration of (total) phosphate in water. At higher concentration of (total) phosphate, concentration of orthophosphate could be limited by the precipitation of Ca-PO_4 solids. This could be one of the reasons behind diminishing inhibiting effect of phosphate in the experimental systems at higher concentrations of phosphate (at phosphate concentration exceeding about 1 mg/l, as discussed above).

4.3 Effect of Zinc on Precipitation of Calcium Carbonate in NaCl Solution

This Section presents the results of the laboratory experiments carried out (in 0.10 M NaCl solutions) to assess the inhibition effect of zinc in delaying or preventing the precipitation of calcium carbonate.

4.3.1 Effect of Zn Concentration

In order to assess the effect of zinc concentration on precipitation of $CaCO_3$, batch experiments were conducted in 0.10 M NaCl solutions, where calcium (Ca) concentration was fixed at 75 mg/l and zinc concentration was varied from zero to 4 mg/l. Two sets of experiments were conducted, one for 30 minutes of mixing time and one for 5 hours of mixing time. Table 4.8(a) and 4.8(b) shows the experimental conditions and the experimental data from these two sets of experiments.

Table 4.8(a): Data from the batch experiments carried out to assess effect of zinc concentration on precipitation of $CaCO_3$ (mixing time: 30 minutes)

Experimental Conditions: Initial Ca^{2+} Concentration: 75 mg/L; Initial total Alkalinity: 200 mg/l as $CaCO_3$; Estimated HCO_3^-: 243.2 mg/l; Estimated CO_3^{2-}: 0.41 mg/l; Mixing time: 30 minutes. Estimated average super-saturation Index (Ω) = 3.1				
Sample No.	pH	Temperature (° C)	Zn^{2+} Conc. (mg/L)	Final Ca^{2+} Concentration (mg/L)
1	7.76	21.0	0	60.8
2	7.65	21.0	0.1	63.2
3	7.71	20.8	0.25	63.2
4	7.57	21.1	0.5	64.0
5	7.67	20.8	0.75	64.0
6	7.6	20.7	1	64.8
7	7.49	20.8	2	66.4
8	7.18	20.7	3	67.2
9	7.32	20.8	4	68.0
Average	7.53	20.87	--	--

Table 4.8(b): Data from the batch experiments carried out to assess effect of zinc concentration on precipitation of $CaCO_3$ (mixing time: 5 hours)

Experimental Conditions:

Initial Ca^{2+} Concentration: 75 mg/L; Initial total Alkalinity: 200 mg/l as $CaCO_{3;}$ Estimated HCO_3^-: 240.9 mg/l; Estimated CO_3^{2-}: 1.51 mg/l; Mixing time: 5 hours. Estimated average super-saturation Index (Ω) = 13.07

Sample No.	pH	Temperature (° C)	Zn^{2+} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	7.95	24.8	0	63.2
2	8.14	24.4	0.1	68.0
3	8.2	24.5	0.25	69.6
4	8.05	24.6	0.5	70.4
5	8.17	24.5	0.75	71.2
6	8.14	24.4	1	72.0
7	8.14	24.6	2	72.8
8	8.08	24.7	3	73.2
9	8.12	24.7	4	73.6
Average	8.10	24.6	--	--

Figure 4.9(a) and 4.9(b) shows concentration of dissolved Ca and precipitated (calculated) Ca, respectively, as a function of zinc concentration. Figure 4.9(a) shows that as phosphate concentration increases, dissolved Ca concentration in water increases; this was observed for two very different mixing times varying by a factor of 10. This means that as zinc concentration increases, precipitation of Ca (as $CaCO_3$) decreases. Figure 4.9(a) shows that up to a zinc concentration of about 1 mg/l, the dissolved Ca concentration increases rapidly with increase in Zn concentration. The effect of phosphate in inhibiting $CaCO_3$ precipitation was more pronounced for a mixing time of 5 hours; the effect of mixing time has been discussed in more detail in Section 4.3.2.

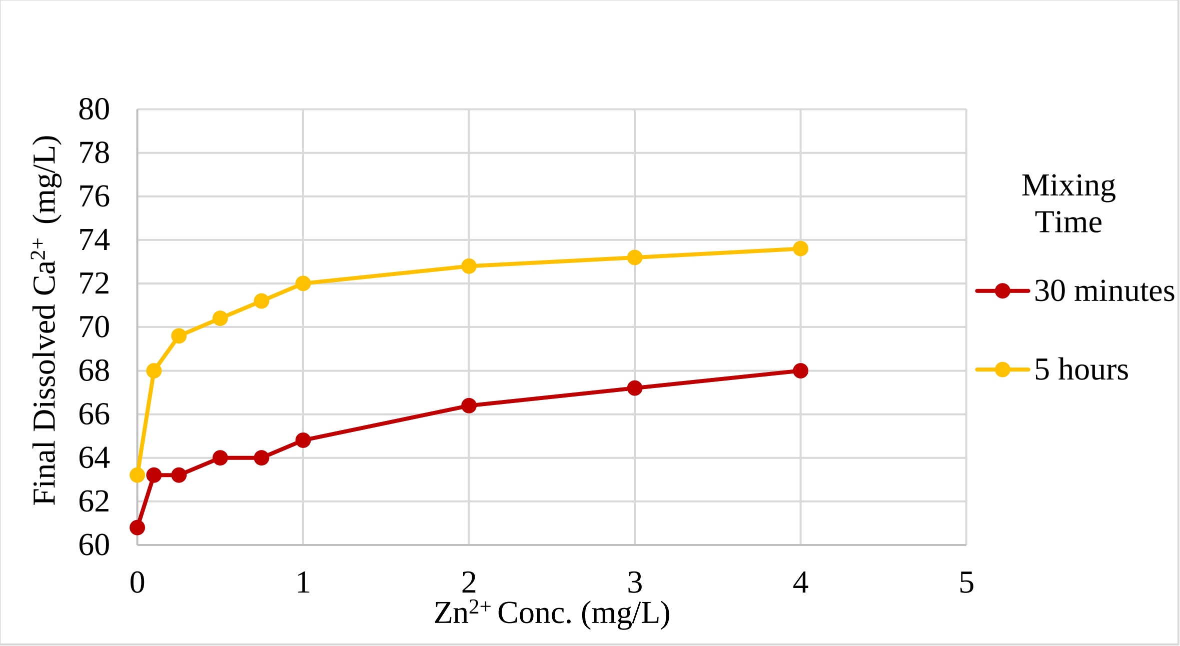


Figure 4.9(a): Concentration of dissolved Ca as a function of zinc concentration (initial Ca = 75 mg/l)

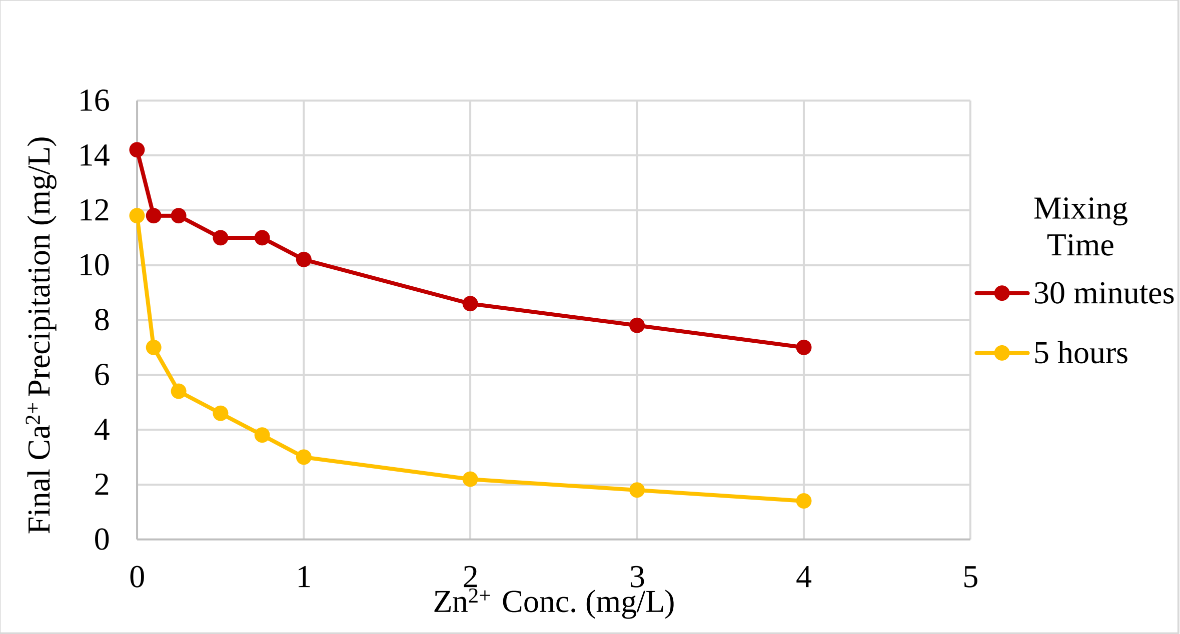


Figure 4.9(b): Concentration of precipitated Ca (calculated) as a function of zinc concentration (initial Ca = 75 mg/l)

Figure 4.9(b) shows calculated precipitated amount of Ca as a function of zinc concentration. It shows that for a particular mixing time, concentration of precipitated Ca decreases as zinc concentration increases. For example, for the batch experiment with 30 minutes of mixing time, amount of precipitated Ca^{2+} was 14.2 mg/l (or 19% of total Ca initially present in water) in the absence of any zinc, while precipitated amount was 7 mg/l (9% of initial Ca) at a zinc concentration of 4 mg/l. For the batch experiment with 5-hour mixing time, amount of precipitated Ca was 11.8 mg/l (or 16% of total Ca initially present in water) in the absence of zinc, while the precipitated amount was only 1.4 mg/l (<2% of initial Ca) in the presence of 4 mg/l zinc. Thus, it is clear that irrespective of mixing time, precipitation of Ca (as $CaCO_3$) decreases as zinc concentration increases; the effect appears to be more pronounced for higher mixing time. It should be noted that for phosphate, the effect was more pronounced at lower mixing time.

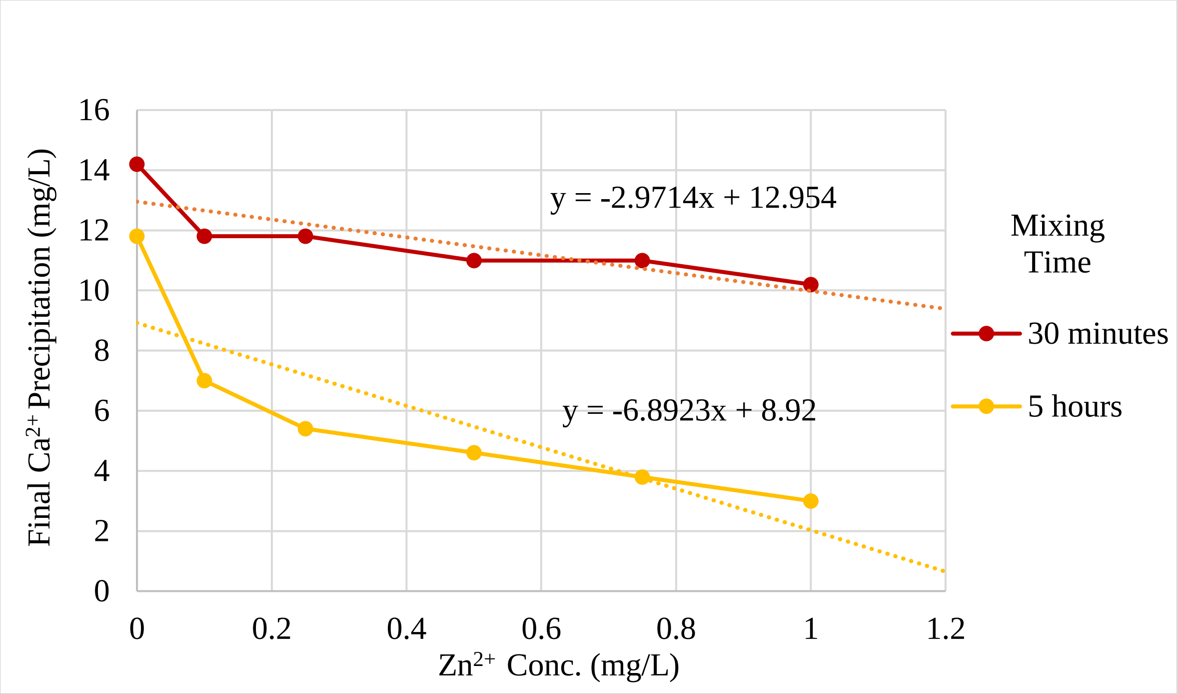


Figure 4.10(a): Concentration of precipitated Ca as a function of zinc concentration for zinc concentration 0 to 1 mg/l, the dotted lines represent the best fit straight line through the experimental data

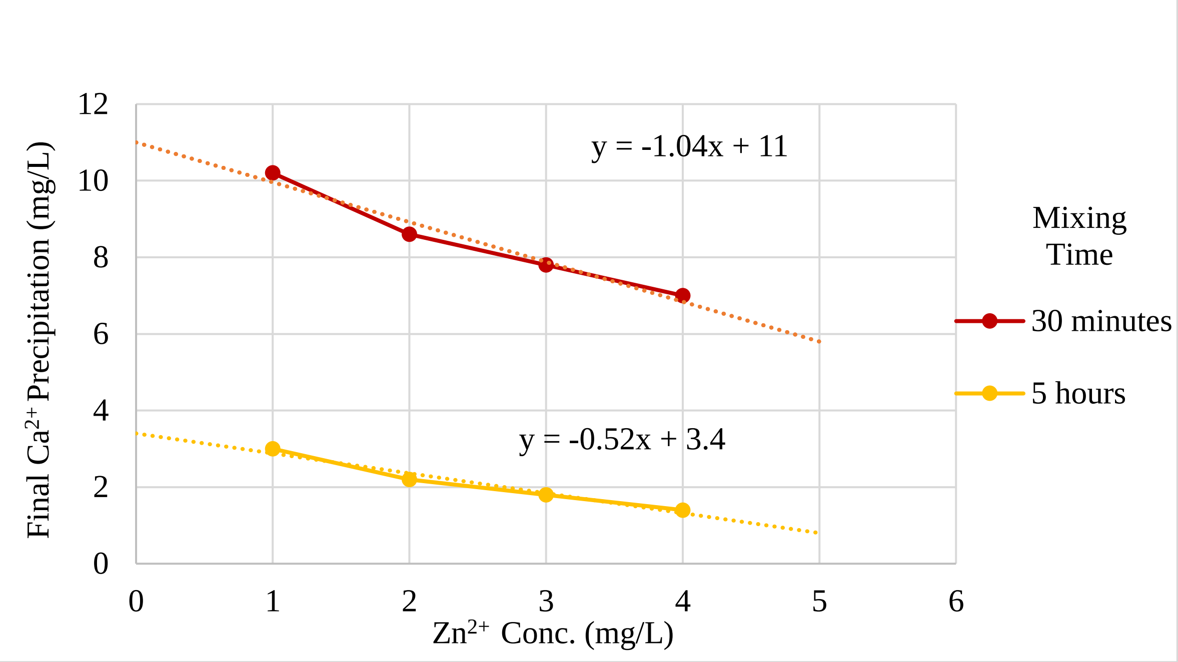


Figure 4.10(b): Concentration of precipitated Ca as a function of zinc concentration for zinc concentration 1 to 4 mg/l, the dotted lines represent the best fit straight line through the experimental data

As observed for phosphate inhibitor, a similar pattern was observed for the effect of Zn concentration on inhibition. As shown in Figs. 4.10(a) and 4.10(b), the effect of zinc in inhibiting precipitation of $CaCO_3$ is more pronounced at lower zinc concentrations. Fig. 4.10(a) shows that up to a zinc concentration of about 1 mg/l, amount of precipitated Ca decreases rapidly as zinc concentration increases; while at higher zinc concentration it decreases at a lower rate. Figure 4.10(a) and Fig. 4.10(b) show estimated average slope of the line representing precipitated Ca versus zinc concentration for zinc concentration. The slopes of the lines represent the decrease of Ca precipitation for unit increase of zinc concentration. A steeper negative slope indicates faster decrease of Ca precipitation and vice versa. Figure 4.10(a) shows a relatively steep negative slope (of about 3 and 6.9) for 30 minutes and 5 hours mixing respectively for zinc concentration up to 1 mg/l; while Fig. 4.10(b) shows a flatter negative slope (0.5 – 1) for zinc concentration greater than 1 mg/l. Thus, effect of zinc concentration in inhibiting Ca precipitation is more pronounced at relatively lower concentrations.

4.3.2 Effect of Mixing Time

This Section presents the results of the batch experiments carried out to assess the effect of mixing time on precipitation of $CaCO_3$ in the presence of phosphate (as an inhibitor). Apart from the experiments with mixing time of 30 minutes and 5 hours (discussed above), two additional experiments were carried out with mixing times of 1 hour and 3 hours; both experiments were carried out in 0.10 M NaCl with initial Ca concentration of 75 mg/l. Table 4.9(a) and 4.9(b) shows the experimental conditions and the experimental data from these two sets of experiments. As noted above, in these experiments nine different zinc concentrations were used, varying from 0 to 4 mg/l.

Table 4.9(a): Data from the batch experiments carried out to assess effect of zinc concentration on precipitation of $CaCO_3$ (mixing time: 1 hour)

Experimental Conditions:

Initial Ca^{2+} Concentration: 75 mg/L; Initial total Alkalinity: 200 mg/l as $CaCO_3$; Estimated HCO_3^-: 242.6 mg/l; Estimated CO_3^{2-}: 0.65 mg/l; Mixing time: 1 hour. Average pH: ~7.75; Average Temperature: ~23 °Celsius

Sample No.	Zn^{2+} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	0	65.6
2	0.1	68.0
3	0.25	69.2
4	0.5	69.6
5	0.75	70.4
6	1	70.8
7	2	71.2
8	3	72.0
9	4	72.8
10	5	73.6

Table 4.9(b): Data from the batch experiments carried out to assess effect of zinc concentration on precipitation of $CaCO_3$ (mixing time: 3 hours)

Experimental Conditions:

Initial Ca^{2+} Concentration: 75 mg/L; Initial total Alkalinity: 200 mg/l as $CaCO_3$; Estimated HCO_3^-: 242.6 mg/l; Estimated CO_3^{2-}: 0.65 mg/l; Mixing time: 1 hour. Average pH: ~7.75; Average Temperature: ~23 °Celsius

Sample No.	Zn^{2+} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	0	68.0
2	0.1	68.8
3	0.25	69.6
4	0.5	71.2
5	0.75	71.2
6	1	71.2
7	2	71.2
8	3	72.8
9	4	73.6
10	5	75.0

Figures 4.11(a, b, c, d, e, f, g, h, i, j) show variation of dissolved Ca concentration as a function of mixing time (0 hour to 5 hours) for all different zinc concentrations used (up to 5 mg/l).

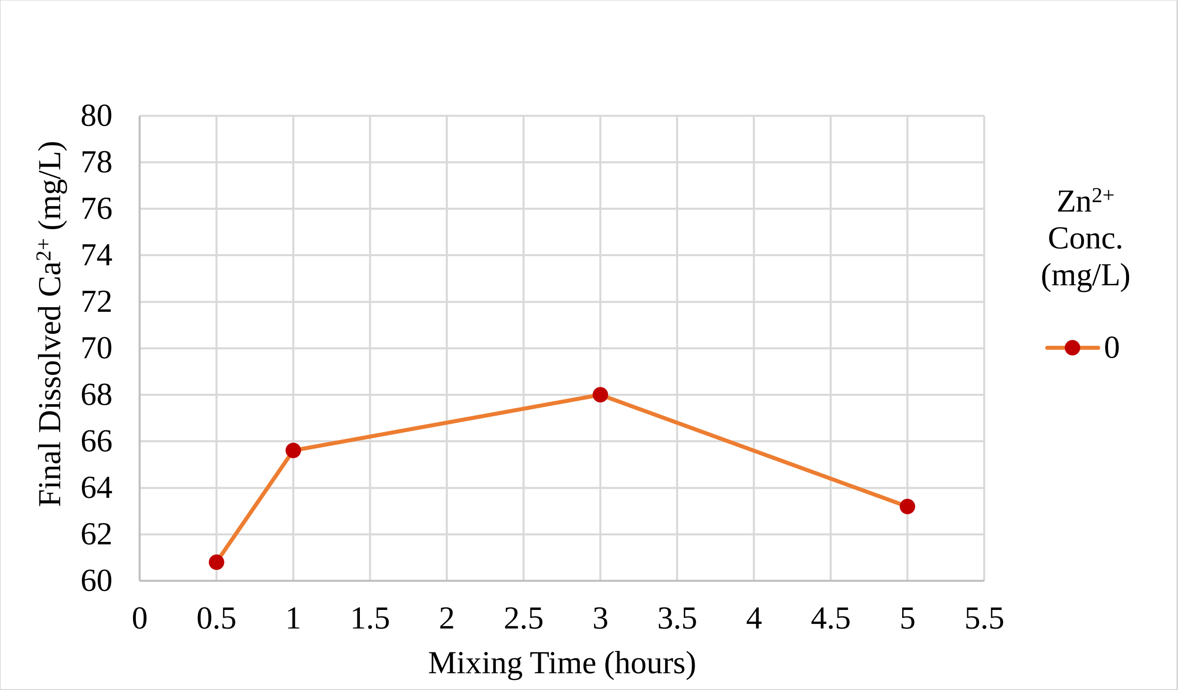


Figure 4.11(a): Final dissolved Ca^{2+} concentration with no inhibitor

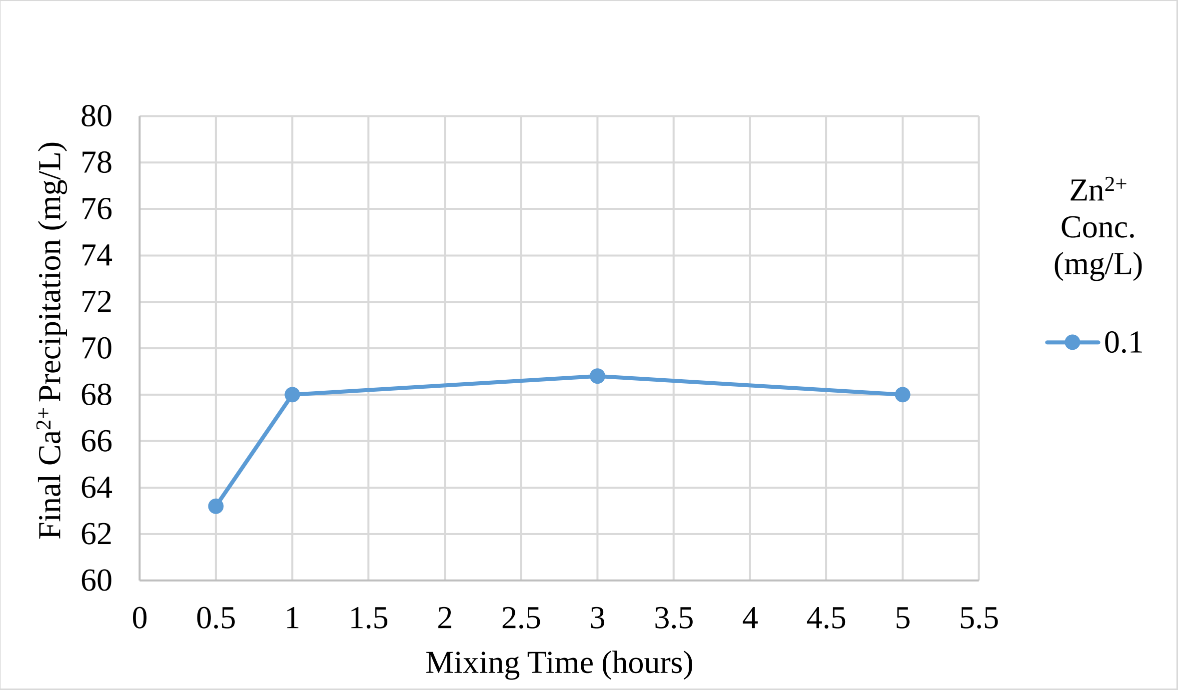


Figure 4.11(b): Final dissolved Ca^{2+} concentration with 0.1 mg/L Zn^{2+} inhibitor

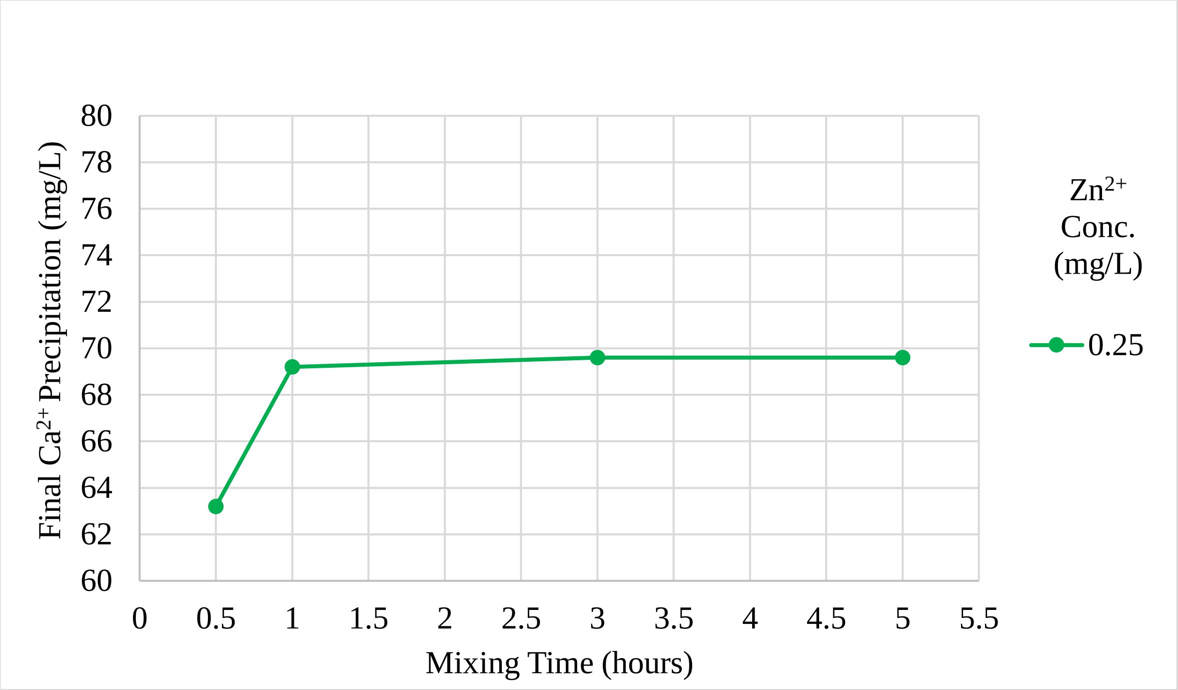


Figure 4.11(c): Final dissolved Ca^{2+} concentration with 0.25 mg/L Zn^{2+} inhibitor

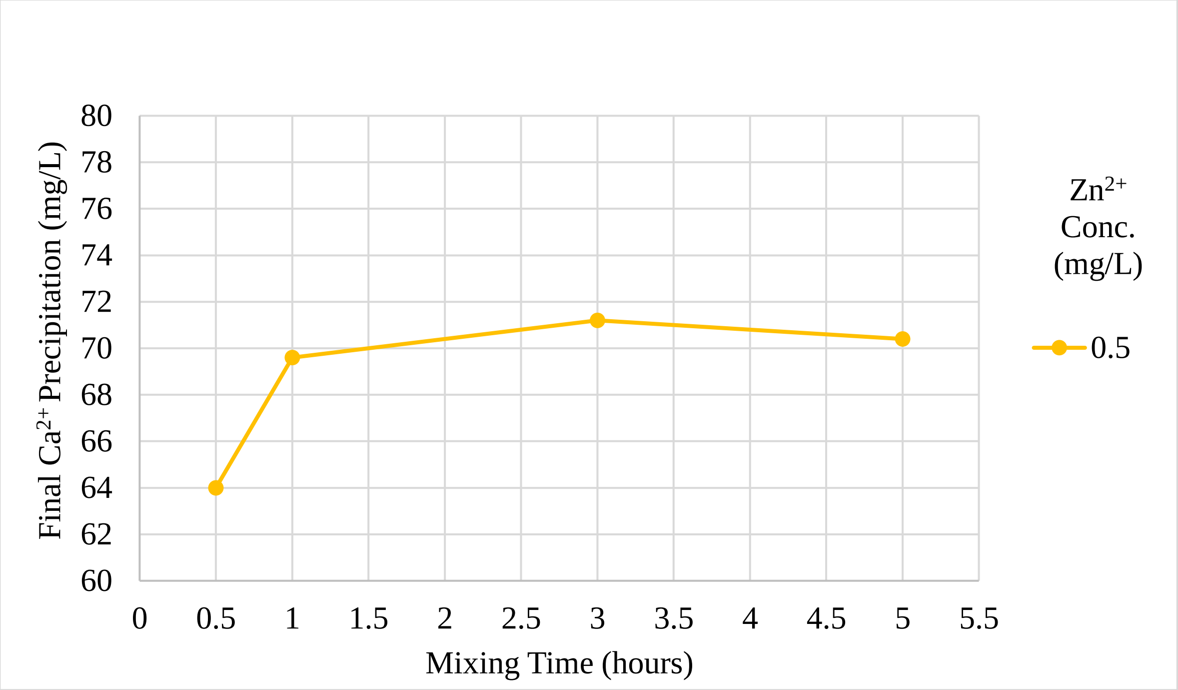


Figure 4.11(d): Final dissolved Ca^{2+} concentration with 0.5 mg/L Zn^{2+} inhibitor

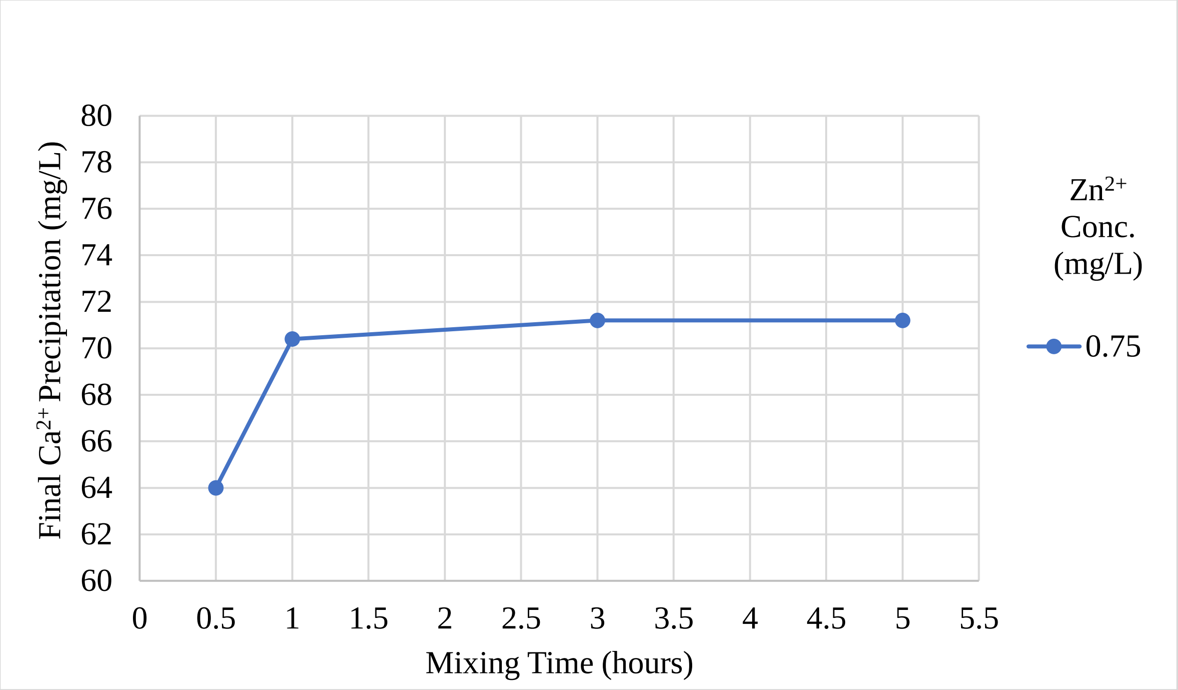


Figure 4.11(e): Final dissolved Ca^{2+} concentration with 0.75 mg/L Zn^{2+} inhibitor

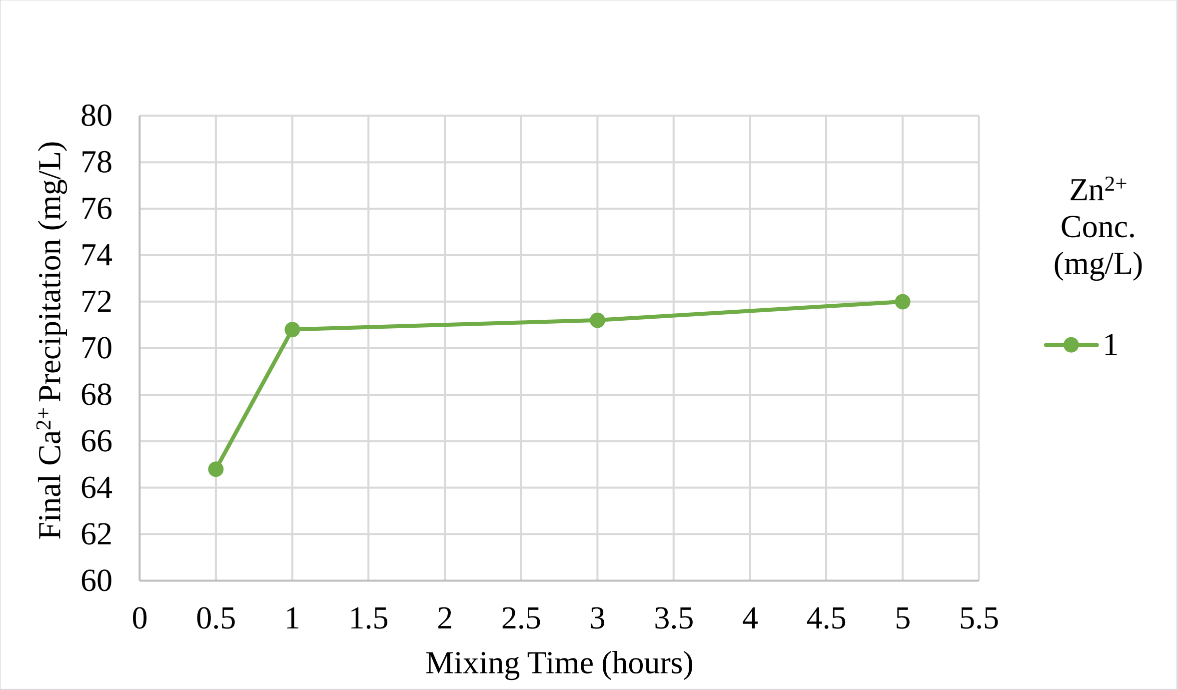


Figure 4.11(f): Final dissolved Ca^{2+} concentration with 1 mg/L Zn^{2+} inhibitor

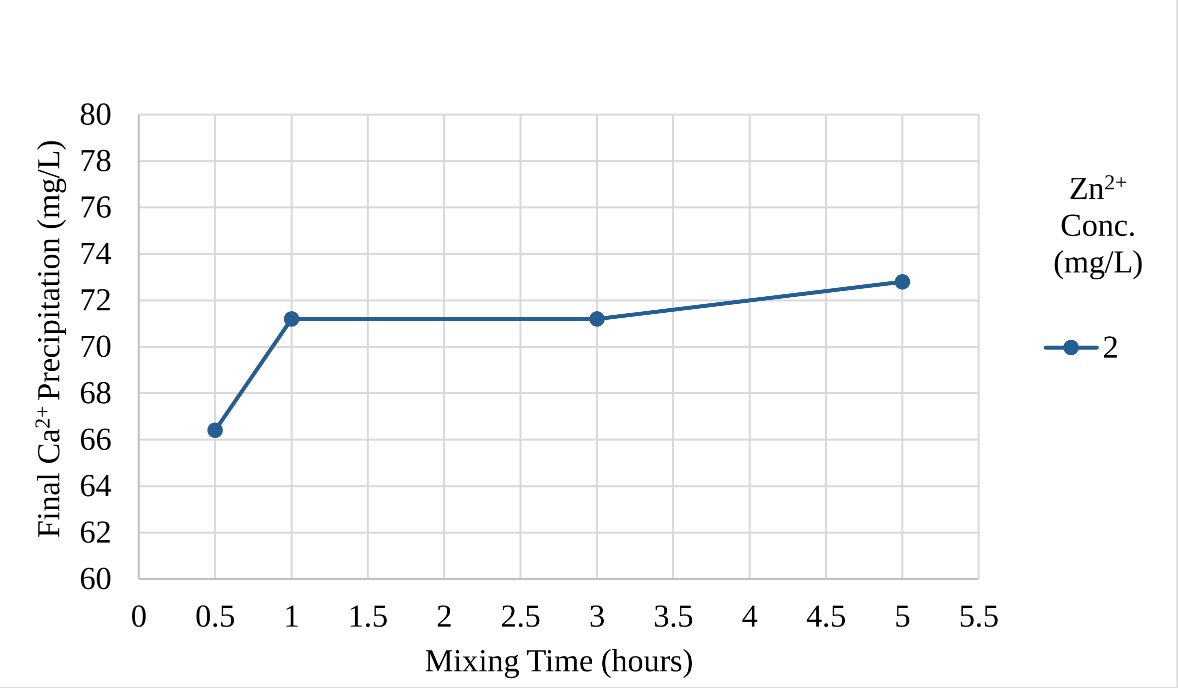


Figure 4.11(g): Final dissolved Ca^{2+} concentration with 2 mg/L Zn^{2+} inhibitor

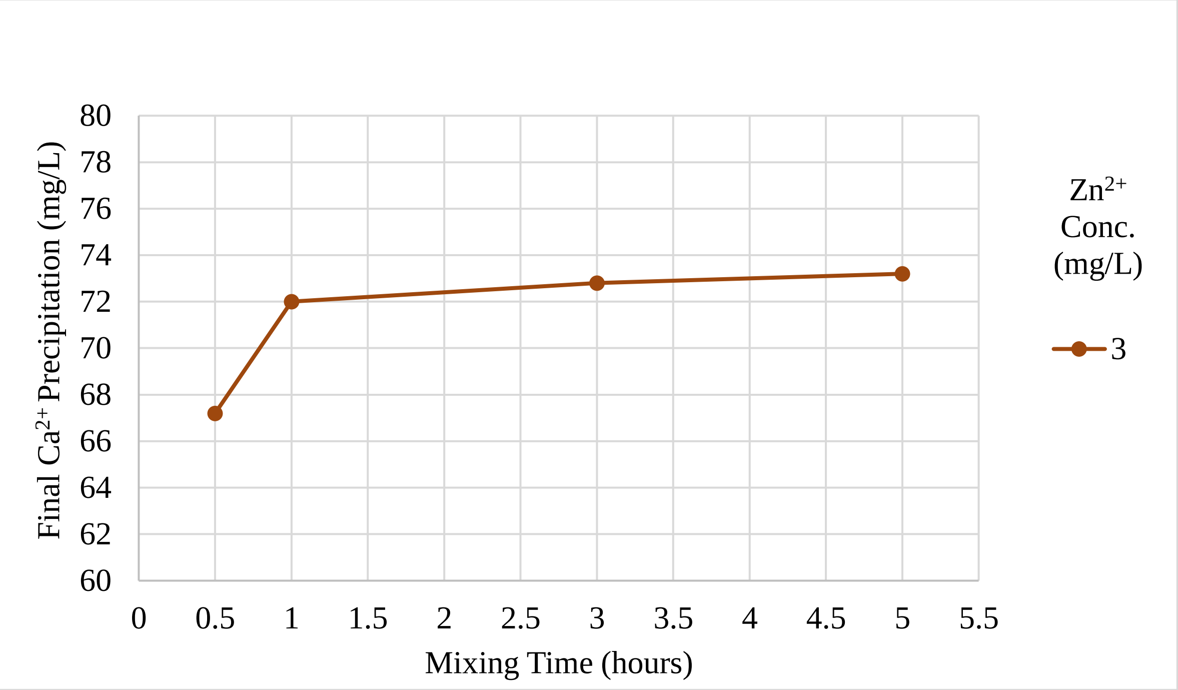


Figure 4.11(h): Final dissolved Ca^{2+} concentration with 3 mg/L Zn^{2+} inhibitor

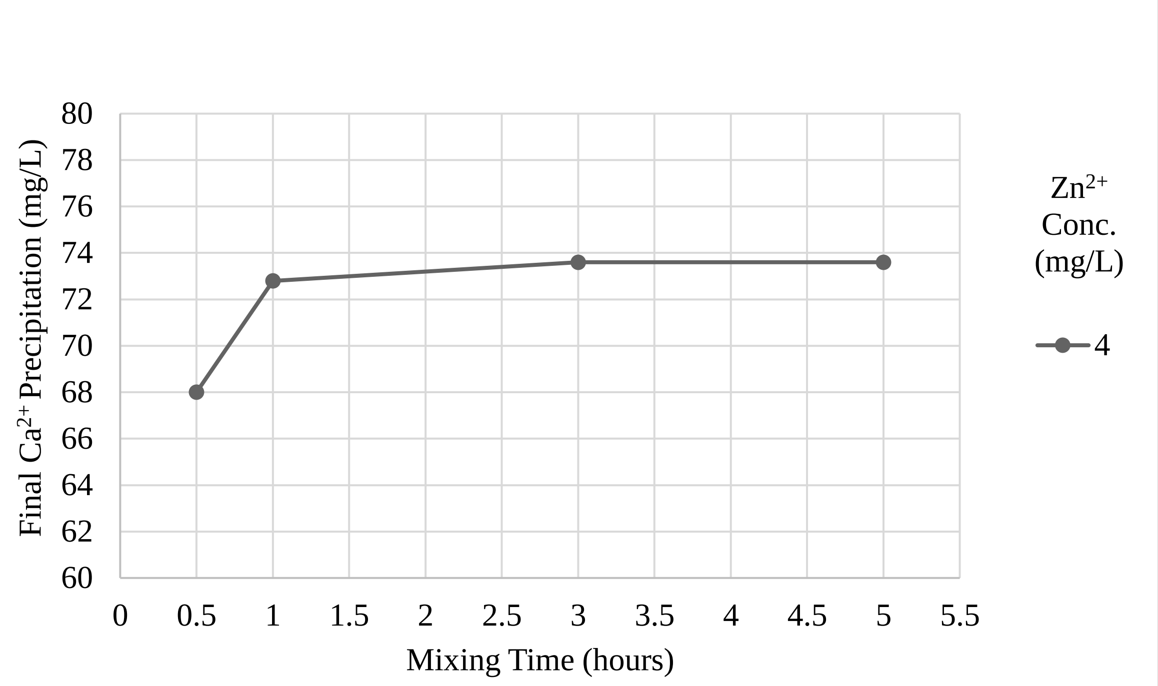


Figure 4.11(i): Final dissolved Ca^{2+} concentration with 4 mg/L Zn^{2+} inhibitor

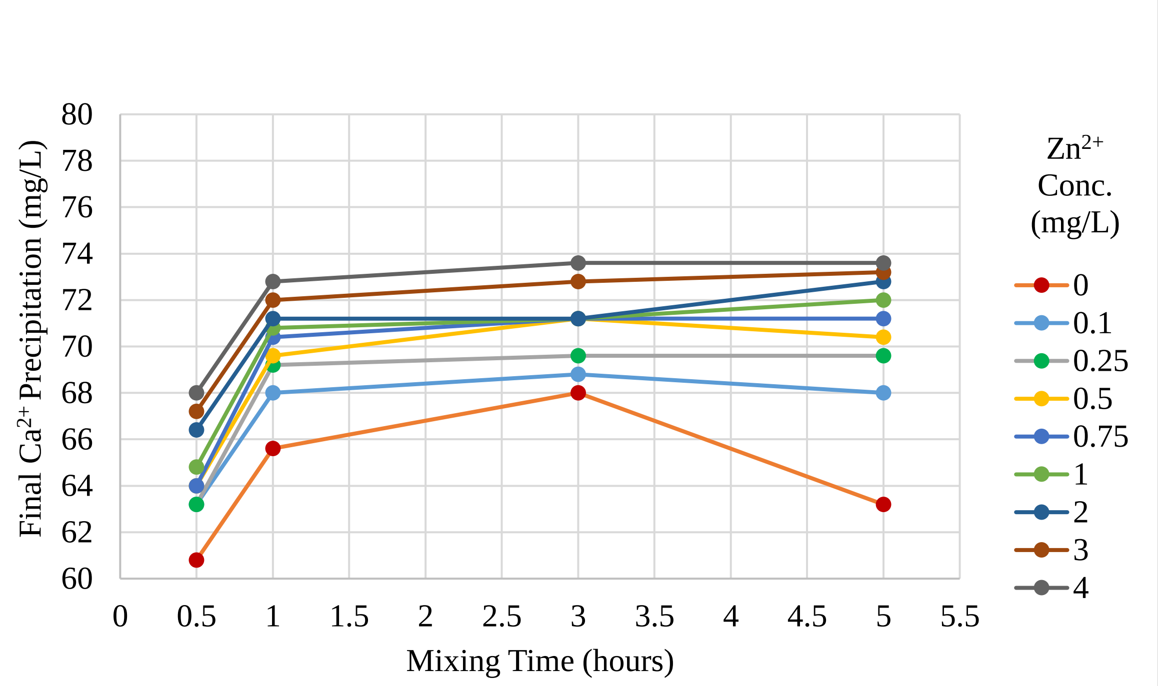


Figure 4.11(j): Final dissolved Ca^{2+} concentration with different concentrations of Zn^{2+} inhibitor

From these figures (Fig. 4.11(a - i)), it can be concluded that for any particular condition, as time increases, the dissolved Ca^{2+} concentration increases. This means that the inhibition effect of Zn increases to some extent with time. For example, for a zinc concentration of 0.5 mg/l, dissolved Ca concentration was 64 mg/l at the end of 0.5 hr, but increased to 70.4 mg/l at the end of 5 hours. Similarly, for a zinc concentration of 0.75 mg/l, dissolved Ca concentration was 64 mg/l at the end of 0.5 hr, but decreased to 71.2 mg/l at the end of 5 hours. The trend was observed for a higher Zn concentration of 4 mg/l; for a zinc concentration of 4 mg/l, dissolved Ca concentration was 68 mg/l at the end of 0.5 hr, but decreases to 73.6 mg/l at the end of 5 hours.

Thus, the effect of mixing time on inhibition effect of phosphate and Zn appears to be somewhat opposite. In case of phosphate, the inhibition effect appears to diminish to some extent with time, while in case of Zn, the inhibition effect appears to become more pronounced with time.

4.3.3 Effect of Degree of Super-saturation

Four sets of experiments were carried out to assess the effect of the degree of super-saturation on the precipitation on calcium carbonate. The experimental conditions of these four sets of experiments, including calculated value of the degree of super-saturation, are summarized in Table 4.10. It shows that the degree of super-saturation in these four sets of experiments varied from 3.10 to 10.06.

Table 4.10: Composition of solution in the batch experiments carried out to assess the effect of degree of saturation on $CaCO_3$ precipitation

Expt. No.	Average pH	Average Temp (°C)	Ca^{2+} (mg/l)	CO_3^{2-} (calculated) (mg/l)	Calculated Ω
5	7.53	20.87	75	1.36	3.10
6	7.59	22.06	100	2.41	4.93
7	7.51	21.62	150	1.71	6.08
8	7.56	24.35	200	7.13	10.06

Notes: (1) All experiments were carried out in 0.10 M NaCl solution;

(2) Mixing time in all experiments = 30 minutes

(3) Alkalinity in all experiments = 200 mg/L

(4) K_{sp} = antilog [-171.9065 – 0.077993*T + $\frac{\mathbf{2839.319}}{\mathbf{T}}$ + 71.595logT]

where T is temperature in Kelvin.

The experimental data for Expt. No. 5 in Table 4.10 are presented in Table 4.8(a); the experimental data for the remaining three experiments (Expt. Nos. 6, 7 and 8) are presented in Table 4.11(a-c).

Table 4.11(a): Data from the Batch Experiment No. 6 (as identified in Table 4.8) with initial Ca concentration of 100 mg/l

Sample No.	pH	Temperature (° C)	Zn^{2+} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	7.55	21.8	0	84.8
2	7.71	21.9	0.1	86.4
3	7.71	21.6	0.25	88.0
4	7.75	21.8	0.5	88.0
5	7.68	22	0.75	88.0
6	7.64	22.3	1	89.6
7	7.58	22.1	2	89.6
8	7.47	22.1	3	91.2
9	7.44	22.1	4	93.6
10	7.35	22.9	5	94.4
Average	7.59	22.1	--	--

Table 4.11(b): Data from the Batch Experiment No. 7 (as identified in Table 4.3) with initial Ca concentration of 150 mg/l

Sample No.	pH	Temperature (° C)	Zn^{2+} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	7.72	21	0	128.0
2	7.76	21.7	0.1	128.8
3	7.65	21.7	0.25	129.6
4	7.63	21.9	0.5	130.4
5	7.53	21.8	0.75	130.4
6	7.52	21.8	1	130.4
7	7.6	21.8	2	130.4
8	7.52	21.8	3	131.2
9	7.0	21.3	4	132.0
10	7.16	21.4	5	132.8
Average	7.51	21.62	--	--

Table 4.11(c): Data from the Batch Experiment No. 8 (as identified in Table 4.3) with initial Ca concentration of 200 mg/l

Sample No.	pH	Temperature (° C)	Zn^{2+} Conc. (mg/L)	Final Dissolved Ca^{2+} (mg/L)
1	7.4	24.4	0	176.0
2	7.56	24.1	0.1	177.6
3	7.6	24.1	0.25	179.2
4	7.65	24.3	0.5	180.8
5	7.65	24.3	0.75	182.4
6	7.67	24.3	1	182.4
7	7.65	24.4	2	184.0
8	7.65	24.5	3	185.6
9	7.45	24.5	4	187.2
10	7.35	24.6	5	188.8
Average	7.56	24.35		

Figure 4.12 shows the calculated precipitated concentration of calcium as a function of zinc concentration for four different degrees of super-saturation. Effort was made to compare the trend of precipitation at different degrees of super-saturation by comparing the slopes of the

lines for each degree of super-saturation. As discussed above in Section 4.2.1, a steeper slope would indicate quicker precipitation with increase in inhibitor (in this case Zn) concentration (and vice versa). The slopes of the lines have been compared for two different ranges of zinc concentration: (a) for zinc concentration up to 1 mg/l; and (b) for zinc concentration from 1 to 5 mg/l. Figure 4.13(a) shows the slopes of the lines for phosphate concentration up to 1 mg/l, while Fig. 4.13(b) shows the slopes of the lines for phosphate concentration of 1 to 5 mg/l.

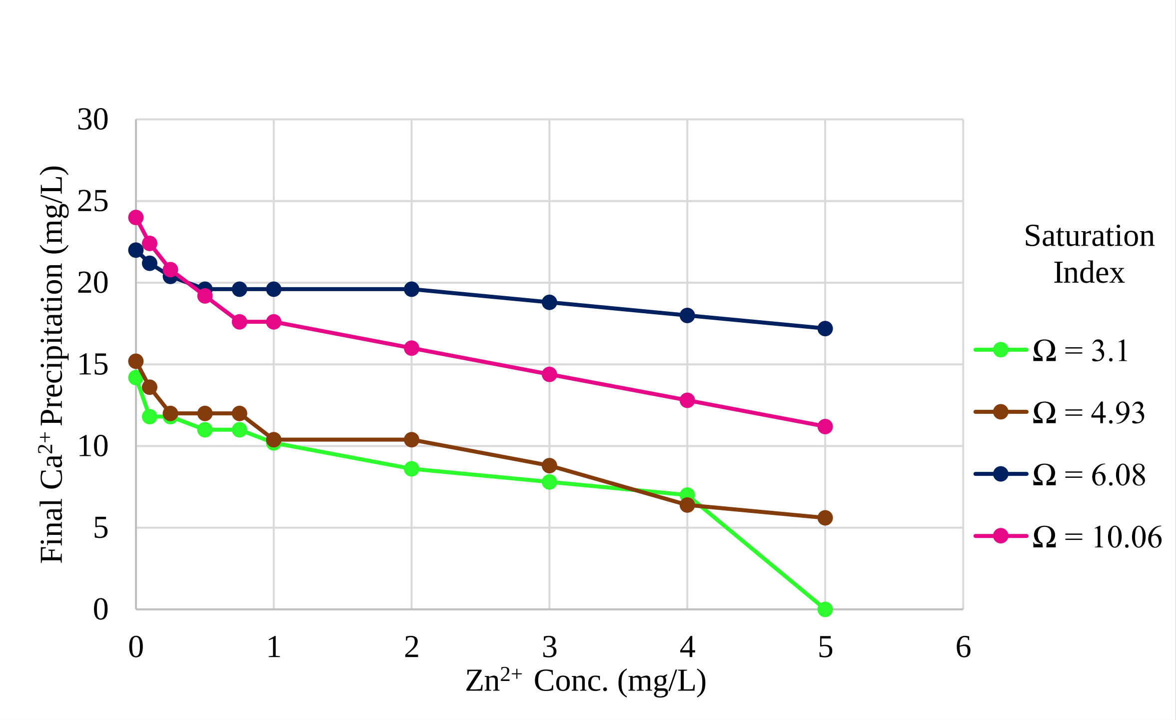


Figure 4.12: Concentration of precipitated Ca^{2+} as a function of zinc concentration for four different degrees of super-saturation

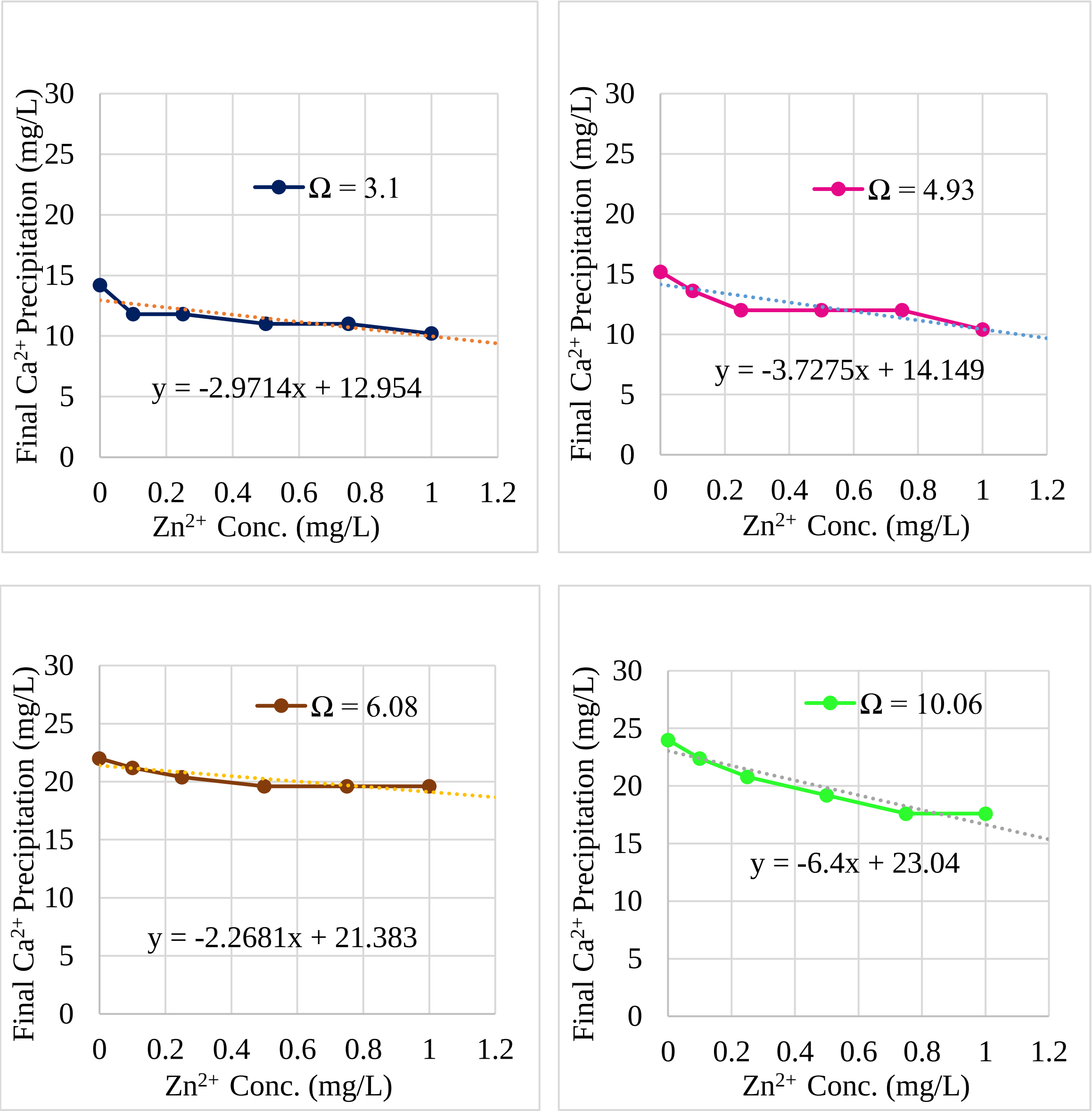


Figure 4.13(a): The slopes of the lines representing precipitated Ca concentration versus zinc concentration for four different degrees of super-saturation (Ω) for zinc concentration upto 1 mg/l

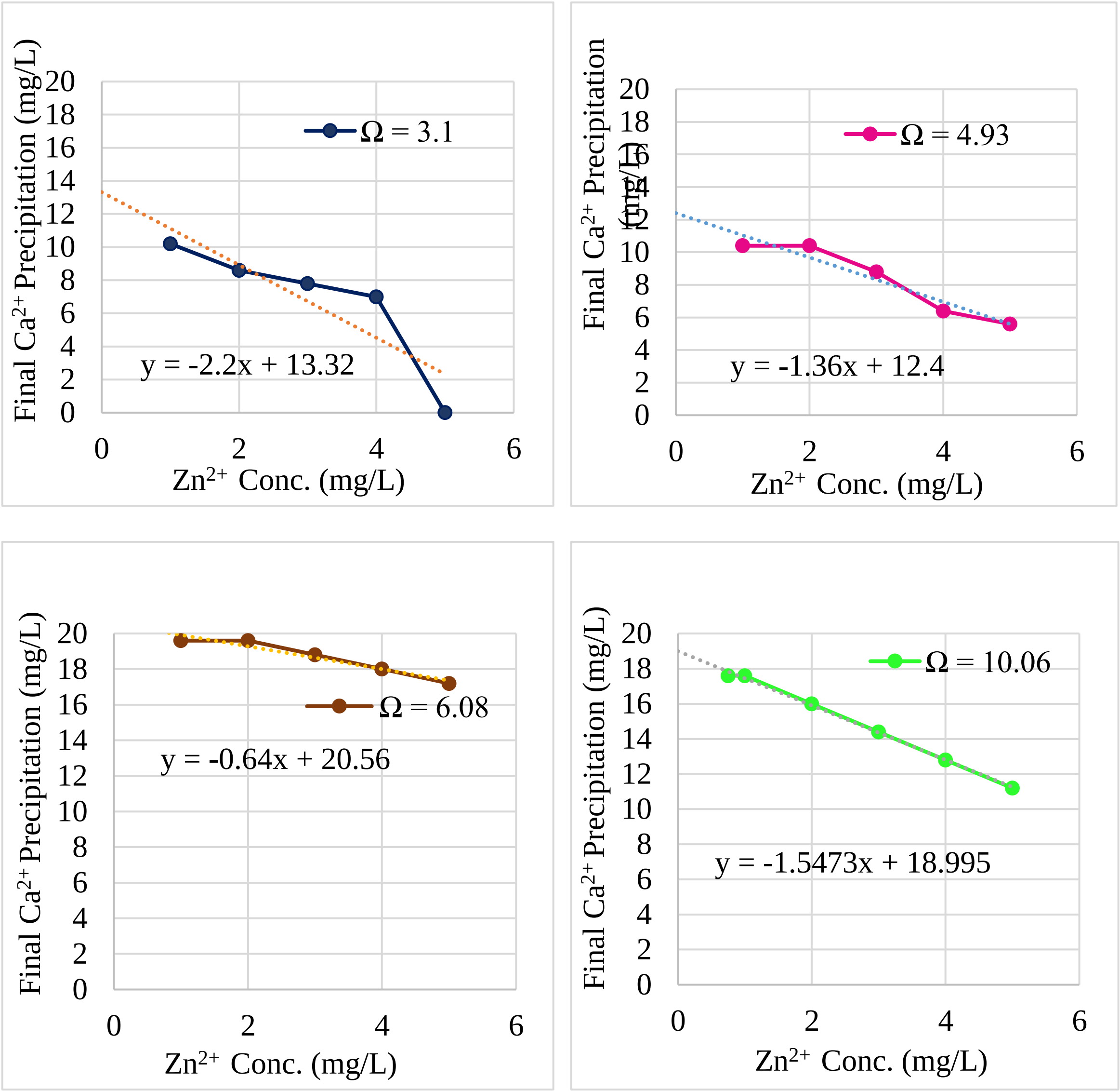


Figure 4.13(b): The slopes of the lines representing precipitated Ca concentration versus phosphate concentration for four different degrees of super-saturation (Ω) for phosphate concentration from 1 mg/l upto 5 mg/l

Table 4.12 lists the slopes of the lines plotted in Fig. 4.13(a) and Fig. 4.13(b). It shows that for all values of degrees of super-saturation, the slope of the lines is steeper between Zn^{2+} concentration of 0.25-1 mg/, while slope if flatter for Zn^{2+} concentration of 1-5 mg/L. The estimated slopes of the lines (shown in Fig. 4.13(a) and 4.13(b)) show that rate of precipitation is higher for lower concentration of Zn (up to 1.0 mg/l), while the rate decreased as Zn concentration increased (irrespective of Ω value). However, the trend was not as evident as it was for phosphate (see Table 4.5). One of the reasons for this could be narrow range of Ω (varying from 3.1 to 10.06) used in experiments with Zn; on the other hand, the range of Ω was much higher (varying from 11.87 to 171.42) for the experiments carried out with phosphate.

Table 4.12: Average slopes of lines for different ranges of zinc concentration for different degrees of super-saturation

Expt. No.	Calculated Ω	Average Slope	
		Zinc = 0-1 mg/l	Zinc = 1-5 mg/l
5	3.10	-2.97	-2.2
6	4.93	-3.73	-1.36
7	6.08	-2.27	-0.64
8	10.06	-6.4	-1.55

4.2.4 MINEQL+ Simulation of Experimental System with Zinc

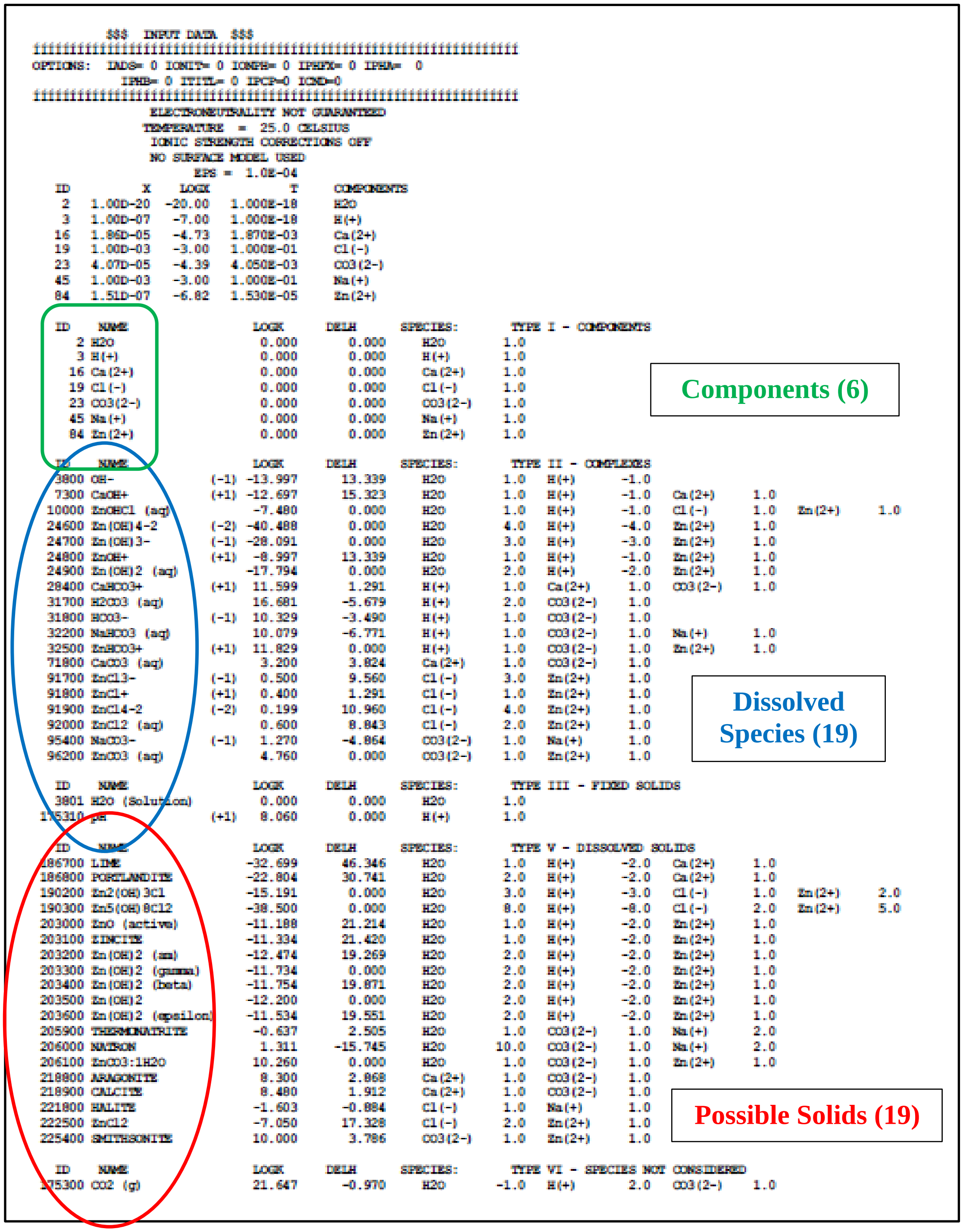
As before, MINEQL+ simulations of the experimental systems were carried out to understand the precipitation of $CaCO_3$(s) under “equilibrium” condition, and how the experimental systems differ from the perfect “equilibrium” system. The following input (“recipe”) was considered for the model simulation:

$(Ca)_T = 1.875 \times 10^{-3}$M (= 75 mg/l)
$(Na)_T = 0.10$ M
$(Cl^-)_T = 0.10$ M
pH = 8.06
Alkalinity = 4.0 meq/L (= 200 mg/l as $CaCO_3$) (“closed system” considered)
$(Zn)_T = 0$ to 7.65×10^{-5} M (0 to 5 mg/l)

The MINEQL+ model input, dissolved species and solids considered (including equilibrium constants) are presented in the Table 4.13. It shows that the model considers 25 dissolved species (including 6 “components” selected for the simulations). The model also considers 19 solids that could possibly form as a result of reactions among the species present within the experimental systems. It should be noted that possible adsorption of Zn^{2+} on $CaCO_3$

crystals was considered in the simulation, because no such reaction has so far been confirmed, and therefore no such reactions are included in the MINEQL+ database.

Table 4.13: MINEQL+ model parameters (components, dissolved species, solids) for simulation of experimental systems in the presence of Zn



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             IPHB= 0 ITITL= 0 IPCP=0 ICND=0
iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii
                  ELECTRONEUTRALITY NOT GUARANTEED
                 TEMPERATURE  =  25.0 CELSIUS
                  IONIC STRENGTH CORRECTIONS OFF
                  NO SURFACE MODEL USED
                        EPS =  1.0E-04
   ID          X      LOGK          T      COMPONENTS
    2   1.00D-20   -20.00   1.000E-18      H2O
    3   1.00D-07    -7.00   1.000E-18      H(+)
   16   1.86D-05    -4.73   1.870E-03      Ca(2+)
   19   1.00D-03    -3.00   1.000E-01      Cl(-)
   23   4.07D-05    -4.39   4.050E-03      CO3(2-)
   45   1.00D-03    -3.00   1.000E-01      Na(+)
   84   1.51D-07    -6.82   1.530E-05      Zn(2+)

   ID     NAME                LOGK      DELH     SPECIES:      TYPE I - COMPONENTS
      2 H2O                  0.000     0.000      H2O        1.0
      3 H(+)                 0.000     0.000      H(+)       1.0
     16 Ca(2+)               0.000     0.000      Ca(2+)     1.0
     19 Cl(-)                0.000     0.000      Cl(-)      1.0
     23 CO3(2-)              0.000     0.000      CO3(2-)    1.0
     45 Na(+)                0.000     0.000      Na(+)      1.0
     84 Zn(2+)               0.000     0.000      Zn(2+)     1.0

   ID     NAME                LOGK      DELH     SPECIES:      TYPE II - COMPLEXES
   3800 OH-            (-1) -13.997    13.339      H2O       1.0  H(+)      -1.0
   7300 CaOH+          (+1) -12.697    15.323      H2O       1.0  H(+)      -1.0  Ca(2+)    1.0
  10000 ZnOHCl (aq)          -7.480     0.000      H2O       1.0  H(+)      -1.0  Cl(-)     1.0  Zn(2+)    1.0
  24600 Zn(OH)4-2      (-2) -40.488     0.000      H2O       4.0  H(+)      -4.0  Zn(2+)    1.0
  24700 Zn(OH)3-       (-1) -28.091     0.000      H2O       3.0  H(+)      -3.0  Zn(2+)    1.0
  24800 ZnOH+          (+1)  -8.997    13.339      H2O       1.0  H(+)      -1.0  Zn(2+)    1.0
  24900 Zn(OH)2 (aq)        -17.794     0.000      H2O       2.0  H(+)      -2.0  Zn(2+)    1.0
  28400 CaHCO3+        (+1)  11.599     1.291      H(+)      1.0  Ca(2+)     1.0  CO3(2-)   1.0
  31700 H2CO3 (aq)           16.681    -5.679      H(+)      2.0  CO3(2-)    1.0
  31800 HCO3-          (-1)  10.329    -3.490      H(+)      1.0  CO3(2-)    1.0
  32200 NaHCO3 (aq)          10.079    -6.771      H(+)      1.0  CO3(2-)    1.0  Na(+)     1.0
  32500 ZnHCO3+        (+1)  11.829     0.000      H(+)      1.0  CO3(2-)    1.0  Zn(2+)    1.0
  71800 CaCO3 (aq)            3.200     3.824      Ca(2+)    1.0  CO3(2-)    1.0
  91700 ZnCl3-         (-1)   0.500     9.560      Cl(-)     3.0  Zn(2+)     1.0
  91800 ZnCl+          (+1)   0.400     1.291      Cl(-)     1.0  Zn(2+)     1.0
  91900 ZnCl4-2        (-2)   0.199    10.960      Cl(-)     4.0  Zn(2+)     1.0
  92000 ZnCl2 (aq)            0.600     8.843      Cl(-)     2.0  Zn(2+)     1.0
  95400 NaCO3-         (-1)   1.270    -4.864      CO3(2-)   1.0  Na(+)      1.0
  96200 ZnCO3 (aq)            4.760     0.000      CO3(2-)   1.0  Zn(2+)     1.0

   ID     NAME                LOGK      DELH     SPECIES:      TYPE III - FIXED SOLIDS
   3801 H2O (Solution)        0.000     0.000      H2O       1.0
 175310 pH             (+1)   8.060     0.000      H(+)      1.0

   ID     NAME                LOGK      DELH     SPECIES:      TYPE V - DISSOLVED SOLIDS
 186700 LIME                -32.699    46.346      H2O       1.0  H(+)      -2.0  Ca(2+)    1.0
 186800 PORTLANDITE         -22.804    30.741      H2O       2.0  H(+)      -2.0  Ca(2+)    1.0
 190200 Zn2(OH)3Cl          -15.191     0.000      H2O       3.0  H(+)      -3.0  Cl(-)     1.0  Zn(2+)    2.0
 190300 Zn5(OH)8Cl2         -38.500     0.000      H2O       8.0  H(+)      -8.0  Cl(-)     2.0  Zn(2+)    5.0
 203000 ZnO (active)        -11.188    21.214      H2O       1.0  H(+)      -2.0  Zn(2+)    1.0
 203100 ZINCITE             -11.334    21.420      H2O       1.0  H(+)      -2.0  Zn(2+)    1.0
 203200 Zn(OH)2 (am)        -12.474    19.269      H2O       2.0  H(+)      -2.0  Zn(2+)    1.0
 203300 Zn(OH)2 (gamma)     -11.734     0.000      H2O       2.0  H(+)      -2.0  Zn(2+)    1.0
 203400 Zn(OH)2 (beta)      -11.754    19.871      H2O       2.0  H(+)      -2.0  Zn(2+)    1.0
 203500 Zn(OH)2             -12.200     0.000      H2O       2.0  H(+)      -2.0  Zn(2+)    1.0
 203600 Zn(OH)2 (epsilon)   -11.534    19.551      H2O       2.0  H(+)      -2.0  Zn(2+)    1.0
 205900 THERMONATRITE        -0.637     2.505      H2O       1.0  CO3(2-)    1.0  Na(+)     2.0
 206000 NATRON                1.311   -15.745      H2O      10.0  CO3(2-)    1.0  Na(+)     2.0
 206100 ZnCO3:1H2O           10.260     0.000      H2O       1.0  CO3(2-)    1.0  Zn(2+)    1.0
 218800 ARAGONITE             8.300     2.868      Ca(2+)    1.0  CO3(2-)    1.0
 218900 CALCITE               8.480     1.912      Ca(2+)    1.0  CO3(2-)    1.0
 221800 HALITE               -1.603    -0.884      Cl(-)     1.0  Na(+)      1.0
 222500 ZnCl2                -7.050    17.328      Cl(-)     2.0  Zn(2+)     1.0
 225400 SMITHSONITE          10.000     3.786      CO3(2-)   1.0  Zn(2+)     1.0

   ID     NAME                LOGK      DELH     SPECIES:      TYPE VI - SPECIES NOT CONSIDERED
 175300 CO2 (g)              21.647    -0.970      H2O      -1.0  H(+)       2.0  CO3(2-)   1.0
```

Components (6)

Dissolved Species (19)

Possible Solids (19)

The model outputs show that under “equilibrium condition”, over 83% of Ca precipitates as $CaCO_3(s)$ (for all Zn concentrations), and Zn has little effect on precipitation of Ca. Predicted dissolved Calcium (Ca^{2+}) concentration was 10.96 mg/l for no Zn, and 11.24 mg/l for the highest Zn concentration of 5 mg/l (7.65×10^{-5} M). On the other hand, in the batch experiments (under similar conditions), dissolved Ca concentration was over 60 mg/l in the absence of Zn, and it increased further in the presence of Zn. Thus, as observed for the simulations with phosphate, a comparison of MINEQL+ simulations and the experimental results clearly show that the formation/precipitation of $CaCO_3(s)$ is limited by the (slow) kinetics of calcium carbonate formation.

Figure 4.14 shows distribution of Ca species for the simulation with Zn concentration of 1.0 mg/l (1.53×10^{-5} M). It shows that Ca^{2+} is the dominant dissolved Ca species, with a concentration of 10.96 mg/l (or 2.74×10^{-3} M). On the other hand, Calcite [$CaCO_3(s)$] is the dominant precipitated form of Ca, with a concentration of 63.2 mg/l (or 1.58×10^{-3} M). The slight increase in dissolved Ca concentration with increasing Zn concentration is due to the formation of $ZnCO_3(s)$ at higher phosphate concentration (as discussed below), which slightly reduces the availability of carbonate for the formation of calcite.

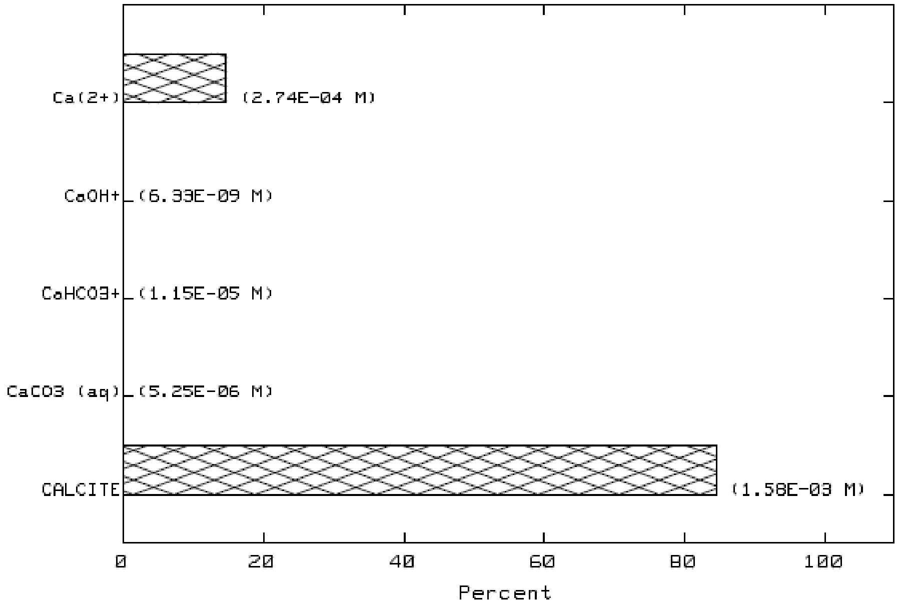
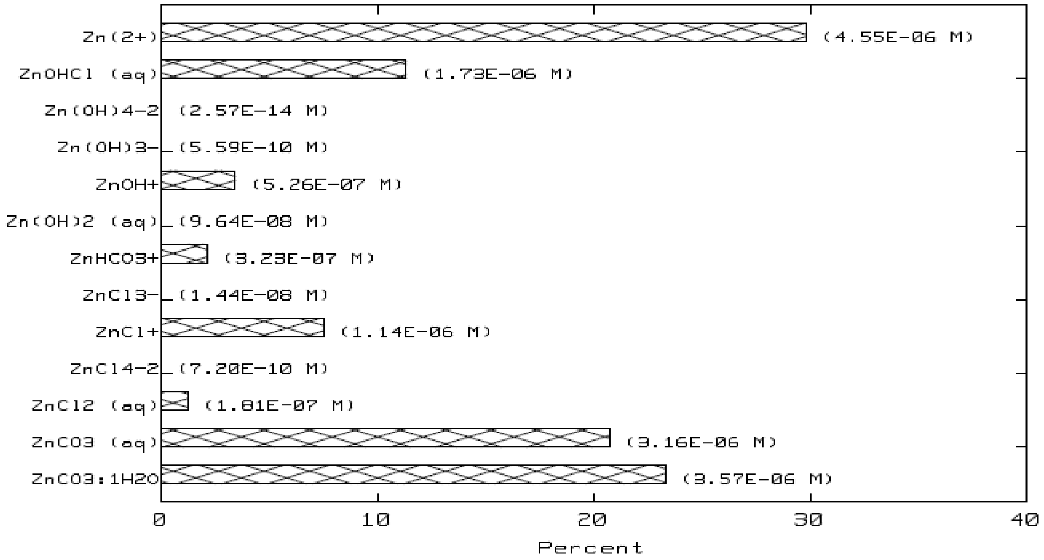


Figure 4.14: Distribution of Ca species in the experimental system with a Zn concentration of 1.0 mg/l (1.53×10^{-5} M)

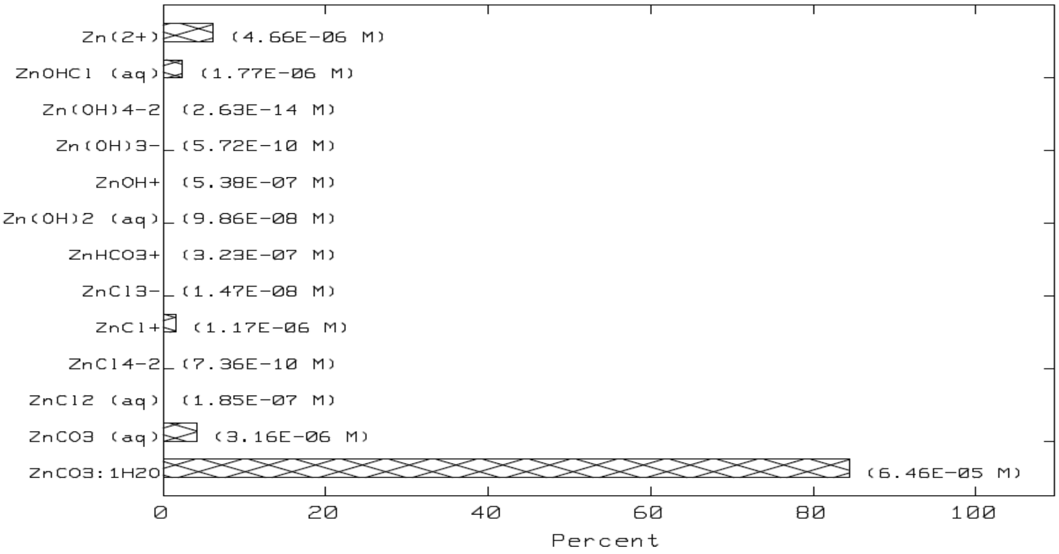
Speciation of Zn Species in Water and its Possible Effects:

Similar to the case for Phosphate, an interesting observation from the model simulations was the distribution of Zn species in the experimental systems under "equilibrium" condition. According to MINEQL+ outputs, at low concentrations of Zn (up to about 1.0 mg/l), Zn remains in water mainly as Zn^{2+}, ZnOHCl, $ZnCl^{+}$, and $ZnCO_3$(aq); and concentrations of these species increase as (total) Zn concentration increases. However, at higher (total) Zn concentrations (≥1 mg/l), $ZnCO_3$(s) begins to form/precipitate, and becomes the dominant species. Figures 4.15(a) and (b) show distribution of Zn species (MINEQL+ output) for the simulations with Zn concentrations of 1.0 mg/l (1.53 x 10^{-5} M) and 5.0 mg/l, respectively. These figures show that as Zn concentration increased, the proportion of dissolved Zn species decreases as $ZnCO_3$(s) precipitates. At a total Zn concentration of 1.0 mg/l, $ZnCO_3$(s) accounts for about 23% of total Zn in water, whereas at a total Zn concentration of 5 mg/l, $ZnCO_3$(s) accounts for about 84% of total Zn in water. Thus, the concentration of dissolved Zn species (including concentration of Zn^{2+}) does not increase proportionate to the concentration of total Zn in the system. Unfortunately, we do not have data on dissolved Zn concentration from our experimental systems to confirm (for deny) the formation of $ZnCO_3$(s) in our experimental systems. However, like other solids, formation/precipitation of $ZnCO_3$(s) is likely to be limited by the kinetics of its formation.

As discussed earlier, the inhibition mechanism of Zn is reported to be the adsorption of orthophosphate on the $CaCO_3$ crystals and the resulting slowing down of crystal growth. In order to evaluate the speciation of Zn in the experimental systems, additional MINEQL+ simulations were carried out, where formation or precipitation of calcium carbonate (both calcite and apatite) was suppressed. Table 4.14 shows the results of model simulations of the experimental system, where formation/precipitation of calcium carbonate was suppressed. It shows that (in the absence of the precipitation of calcium carbonate), Ca^{2+} is the dominant Ca species in the system; the slight increase in Ca^{2+} concentration at higher Zn concentration is due to the precipitation of $ZnCO_3$(s). The last column of Table 4.14 shows the simulated concentrations of Zn^{2+} in the experimental systems. It shows that Zn concentration initially increases (almost proportionately) with increasing concentration of Zn (up to a zinc concentration of about 1.0 mg/l); however, as Zn concentration increases further, $ZnCO_3$(s) begins to form, which limits the increase of concentration of dissolved Zn species (including Zn^{2+}). Figure 4.16 shows variation of Zn^{2+} concentration as a function of total Zn concentration; it shows a plateauing Zn^{2+} concentration with increasing total Zn concentration.



(a) Total Zn = 1.0 mg/l (1.53 x 10^{-5} M)



(b) Total Zn = 5.0 mg/l (7.65 x 10^{-5} M)

Figure 4.15: Distribution of Zn species in the experimental system with Zn: (a) Total Zn = 1.0 mg/l (1.53 x 10^{-5} M); (b) Total Zn = 5.0 mg/l (7.65 x 10^{-5} M)

Table 4.14: Results of MINEQL+ simulations, where formation/precipitation of calcium carbonate was suppressed [Model system: $(Ca)_T = 1.875 \times 10^{-3}$M (= 75 mg/l); $(Na)_T = 0.10$ M; $(Cl^-)_T = 0.10$ M; pH = 8.06; Alkalinity = 4.0×10^{-3} eq/L (= 200 mg/l as $CaCO_3$)]

Model Run No.	Total Zinc	Ca^{2+} [M]	Zn^{2+} [M]
1	0 M (0 mg/l)	1.71×10^{-3}	--
2	1.53×10^{-6} M (0.10 mg/l)	1.71×10^{-3}	5.05×10^{-7}
3	3.82×10^{-6} M (0.25 mg/l)	1.71×10^{-3}	1.26×10^{-6}
4	7.64×10^{-6} M (0.50 mg/l)	1.71×10^{-3}	2.52×10^{-6}
5	1.147×10^{-5} M (0.75 mg/l)	1.71×10^{-3}	2.87×10^{-6}
6	1.53×10^{-5} M (1.0 mg/l)	1.71×10^{-3}	2.87×10^{-6}
7	3.06×10^{-5} M (2.0 mg/l)	1.71×10^{-3}	2.89×10^{-6}
8	4.59×10^{-5} M (3.0 mg/l)	1.71×10^{-3}	2.90×10^{-6}
9	6.12×10^{-5} M (4.0 mg/l)	1.71×10^{-3}	2.91×10^{-6}
10	7.65×10^{-5} M (5.0 mg/l)	1.71×10^{-3}	2.92×10^{-6}

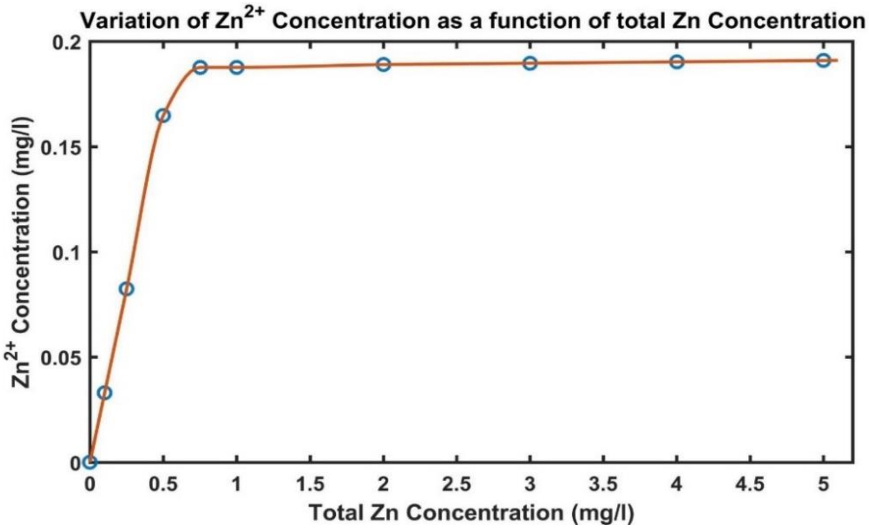


Figure 4.16: Variation of Zn^{2+} concentration as a function of total Zn concentration (from model simulations)

Figures 4.17(a) – (c) show speciation of Zinc at three different total Zn concentrations. These figures show that with increasing (total) Zn concentration, the concentration of dissolved Zn species decrease and the concentration of $ZnCO_3$(s) increases. Thus, the model simulations suggest that, in the presence of a carbonate system, Zn would tend to precipitate $ZnCO_3$(s) under favorable conditions, especially at higher Zn concentrations. So, concentration of dissolved Zn species, including Zn^{2+} (which is apparently responsible for the inhibition effect of phosphate) would not increase proportionately to the total concentration of (total) Zn in water. At higher concentration of (total) Zn, concentration of Zn^{2+} could be limited by the precipitation of $ZnCO_3$(s). This could be one of the reasons behind diminishing inhibiting effect of Zn in the experimental systems at higher concentrations of Zn concentrations (at total Zn concentration exceeding about 1 mg/l, as discussed above).

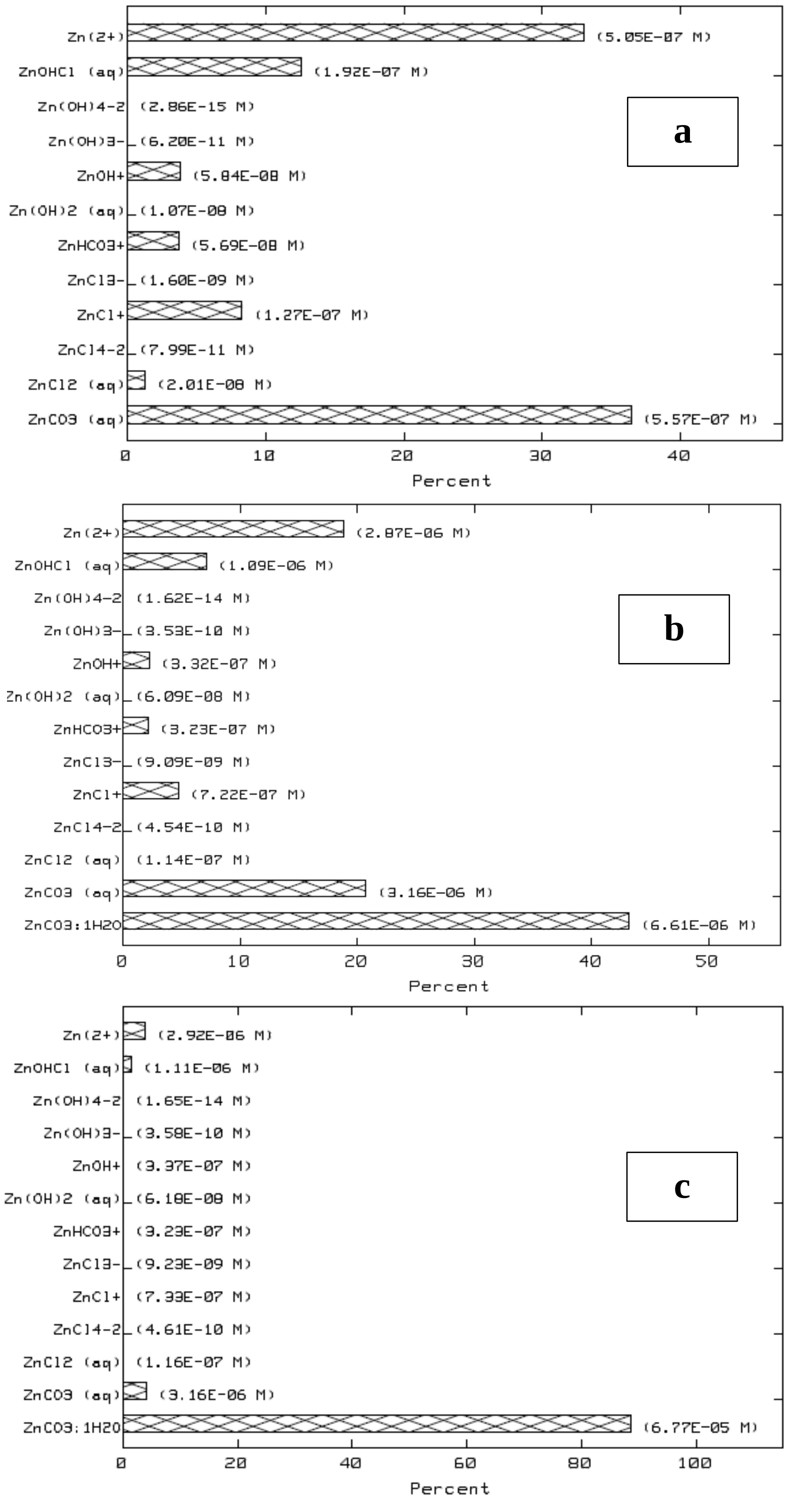


Figure 4.17: MINEQL+ outputs showing distribution of phosphate species in the experimental systems for: (a) Zn = 0.10 mg/l (1.53 x 10^{-6} M); (b) Zn = 1.0 mg/l (1.53 x 10^{-5} M); (c) Zn = 5.0 mg/l (7.65 x 10^{-5} M)

4.4 Comparison of Phosphate and Zinc as Inhibitor in NaCl Solutions

This Section presents the comparison of Zn and phosphate as inhibitor in delaying the precipitation of $CaCO_3$.

In order to compare the effect of phosphate and zinc inhibitor concentration on precipitation of $CaCO_3$, the results of the batch experiments carried out with initial Ca concentration of 75 mg/l and inhibitor (either phosphate or Zn) concentration varying from 0 to 5 mg/l have been plotted on the same graph for different mixing times. These experiments carried out with phosphate and Zn as inhibitor were almost identical, except that for batch experiments with phosphate, Ω varied from about 11.9 to 22.2; while for experiments with Zn, Ω varied from about 3.1 to 13.1.

Figure 4.18 (a) to (d) shows dissolved concentration of Ca as a function of the concentration of the inhibitor (phosphate and Zn) for four different mixing times: (a) 30 minutes; (b) 1 hour; (c) 3 hours, and (d) 5 hours. These figures show (as discussed above) that the inhibition effect of both inhibitors (i.e., Zn and phosphate) increases with increasing concentration of the inhibitor. But these four figures provide a very interesting observation regarding the inhibition effect of Zn and phosphate on precipitation of $CaCO_3$. Figure 4.18(a) shows that for 30 minutes mixing time, the inhibition effect of phosphate is higher than that of Zn (because concentration of dissolved Ca in the system was higher in the presence of phosphate, compared to those in the presence of Zn). As shows in Fig 4.18(b), the inhibition effect of phosphate and Zn became almost same for 1 hour mixing time. As the mixing time increased further, the inhibition effect of Zn became stronger than that of phosphate, as shown in Fig. 4.18 (c) and Fig. 4.18 (d). Thus, it appears that over longer period of time, Zn would be more effective in preventing/delaying precipitation of $CaCO_3$, compared to phosphate. Effectiveness of longer period of time is important for preventing precipitation in water distribution system, since the supplied water could remain in the distribution system for hours before being delivered at the consumer end.

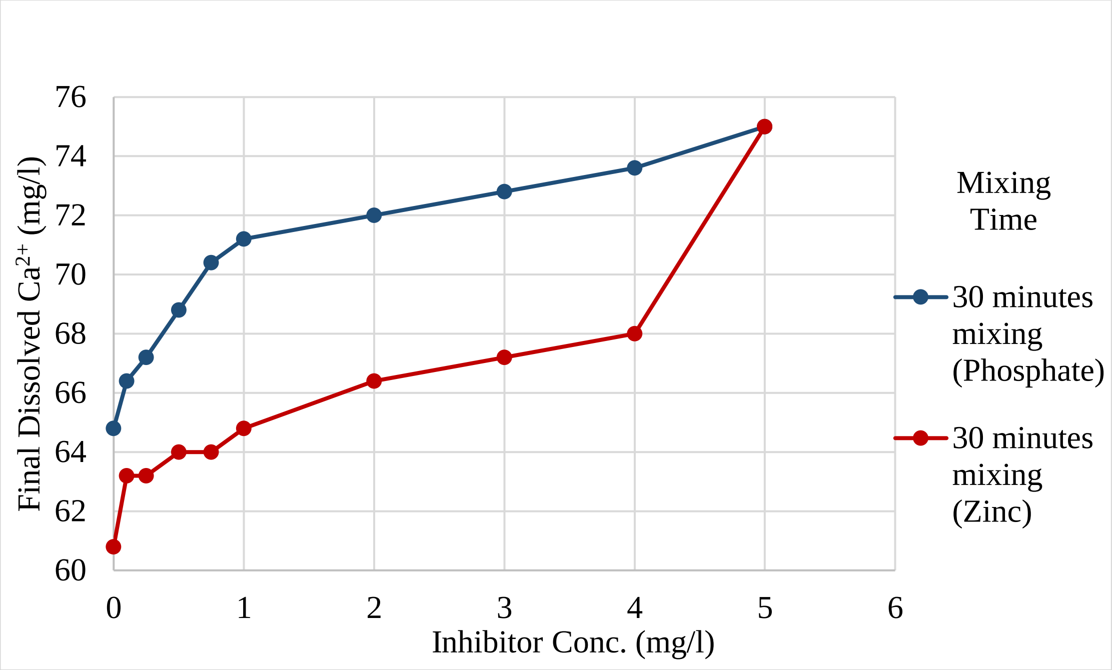


Figure 4.18(a): Concentration of dissolved Ca (initial Ca = 75 mg/l) as a function of inhibitor (Zn and phosphate) concentration for a mixing time of 30 minutes

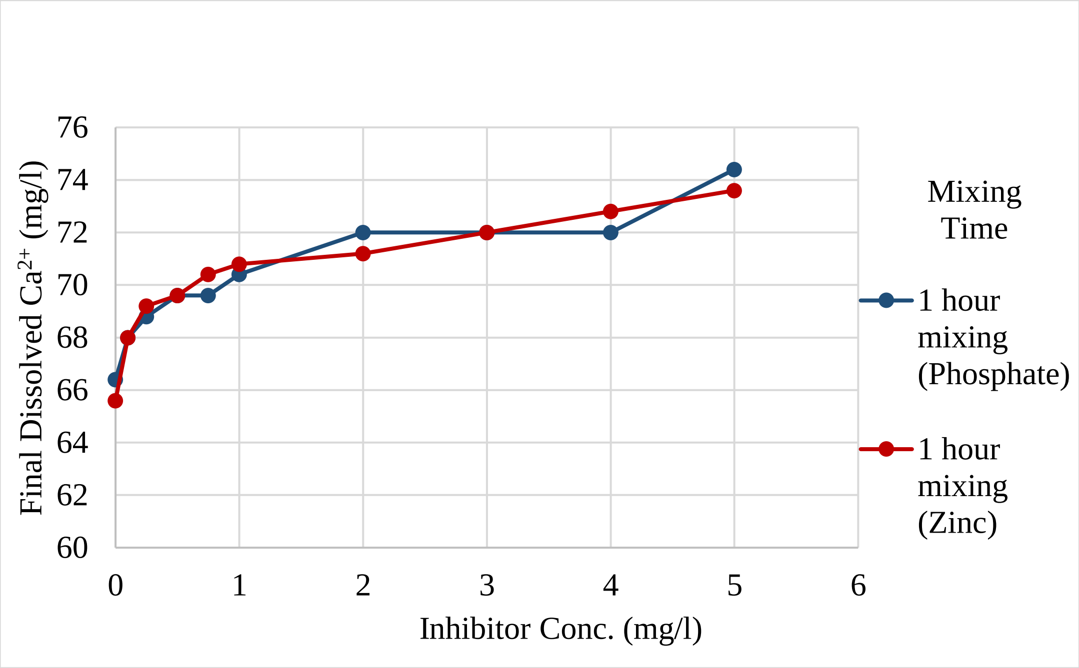


Figure 4.18(b): Concentration of dissolved Ca (initial Ca = 75 mg/l) as a function of inhibitor (Zn and phosphate) concentration for a mixing time of 1 hour

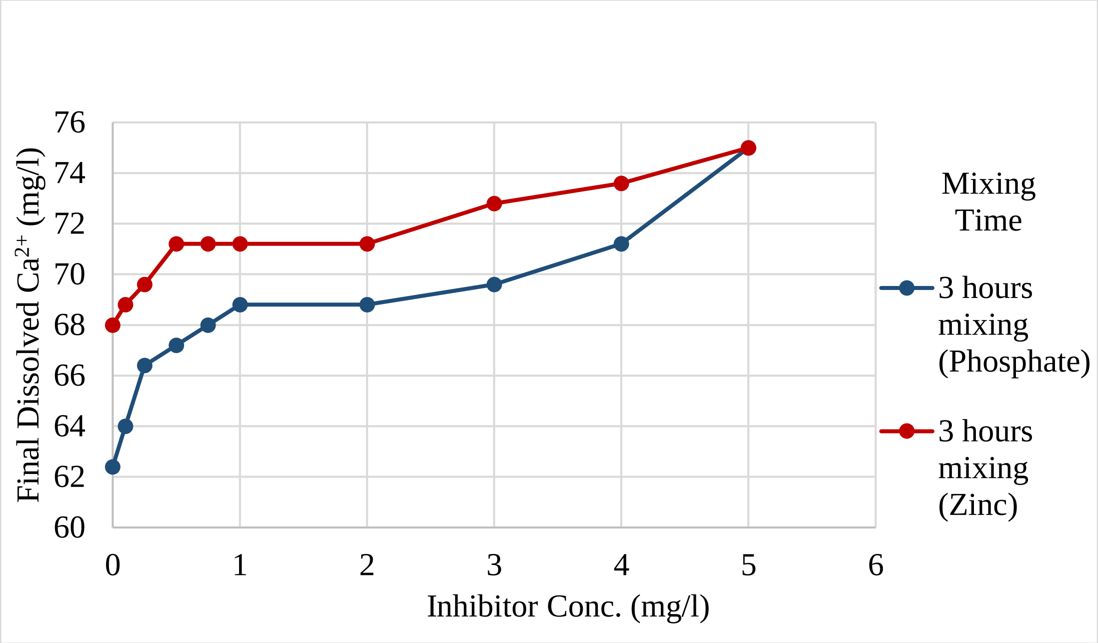


Figure 4.18(c): Concentration of dissolved Ca (initial Ca = 75 mg/l) as a function of inhibitor (Zn and phosphate) concentration for a mixing time of 3 hour

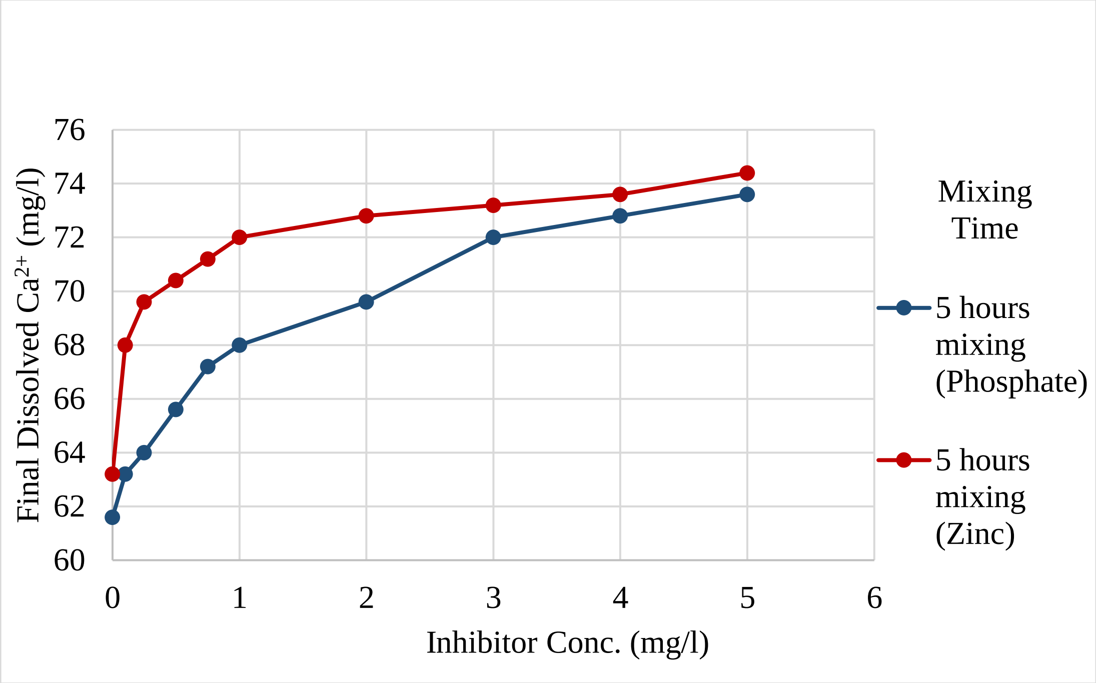


Figure 4.18(d): Concentration of dissolved Ca (initial Ca = 75 mg/l) as a function of inhibitor (Zn and phosphate) concentration for a mixing time of 5 hour

In order to better understand the effect of time on the inhibition effect of Zn and phosphate, the data (presented above) of the batch experiments were further analyzed. Figures 4.19(a) - 4.19(i) show the comparison of dissolved Ca concentration as a function of time, for different Zn/phosphate concentration. These figures show that for an inhibitor concentration of up to about 2 mg/l [Figures 4.19(a) – (f)], dissolved Ca concentration increases with time in the presence of Zn, while it decreases with time in the presence of phosphate. Higher dissolved concentration of Ca means lower precipitation of $CaCO_3$. In other words, we can say that the inhibition effect of Zn increases with time, while that of phosphate decreases with time. This trend, however, diminishes at higher inhibitor concentrations, as shown in Figures 4.19(g) – (h). At an inhibitor (Zn/phosphate) concentration of 4 mg/l, there is negligible change of concentration of dissolved Ca with time. These figures therefore suggest that the effect of time on inhibition effect of Zn and phosphate is more pronounced at lower concentrations (up to about 1 mg/l) of inhibitors.

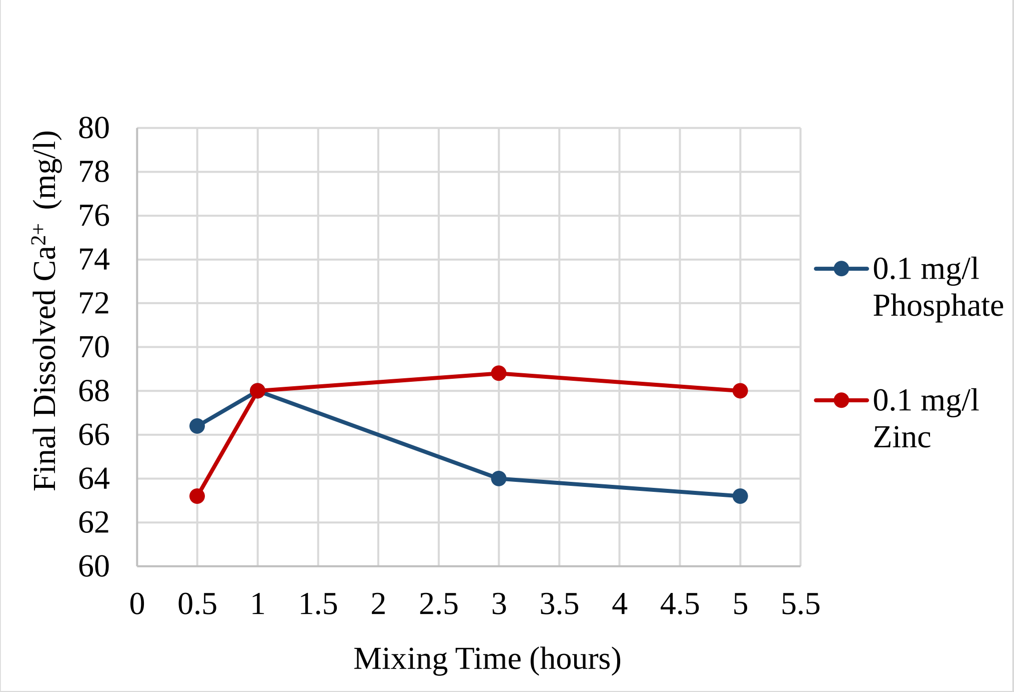


Figure 4.19(a): Final dissolved Ca^{2+} concentration as a function of mixing time for inhibitor (i.e., Zn and phosphate) concentration of 0.1 mg/L

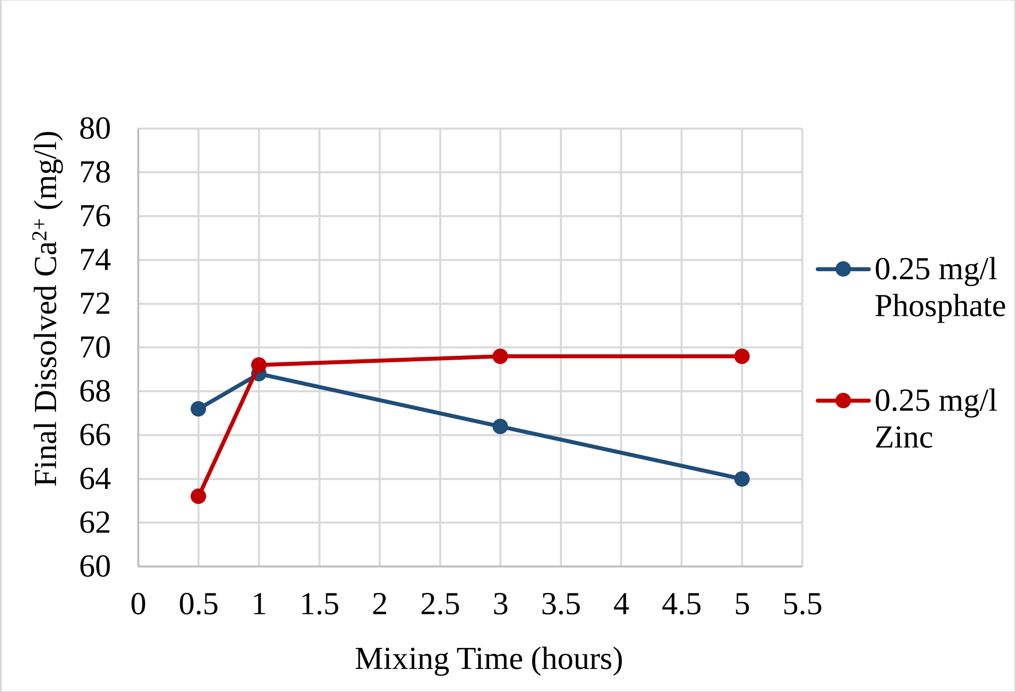


Figure 4.19(b): Final dissolved Ca^{2+} concentration as a function of mixing time for inhibitor (i.e., Zn and phosphate) concentration of 0.25 mg/L

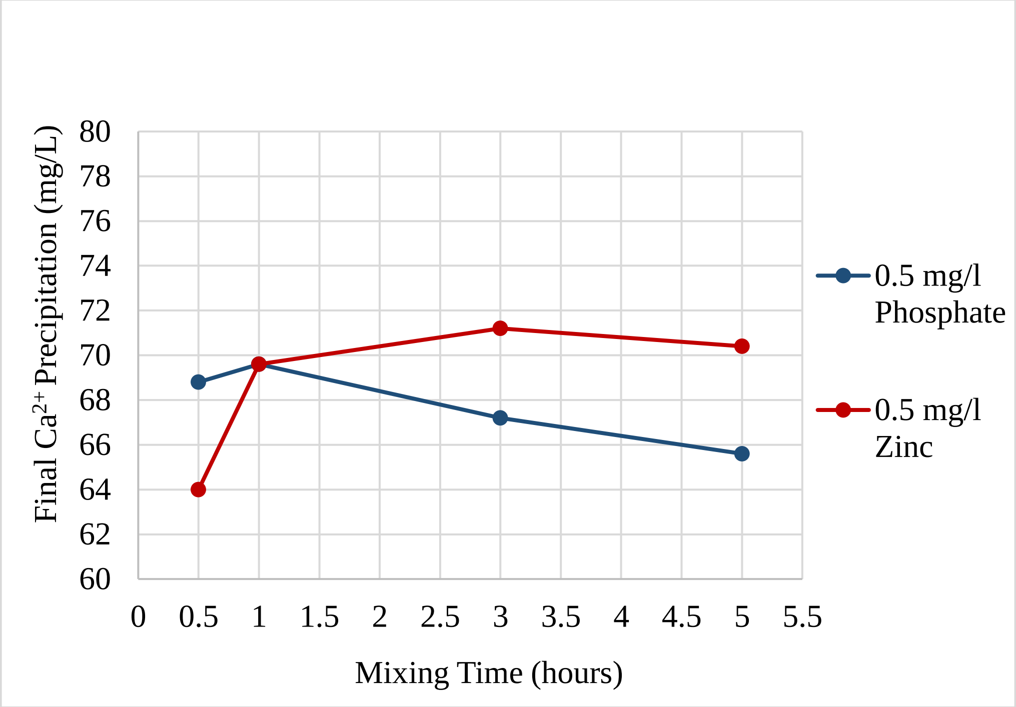


Figure 4.19(c): Final dissolved Ca^{2+} concentration as a function of mixing time for inhibitor (i.e., Zn and phosphate) concentration of 0.5 mg/L

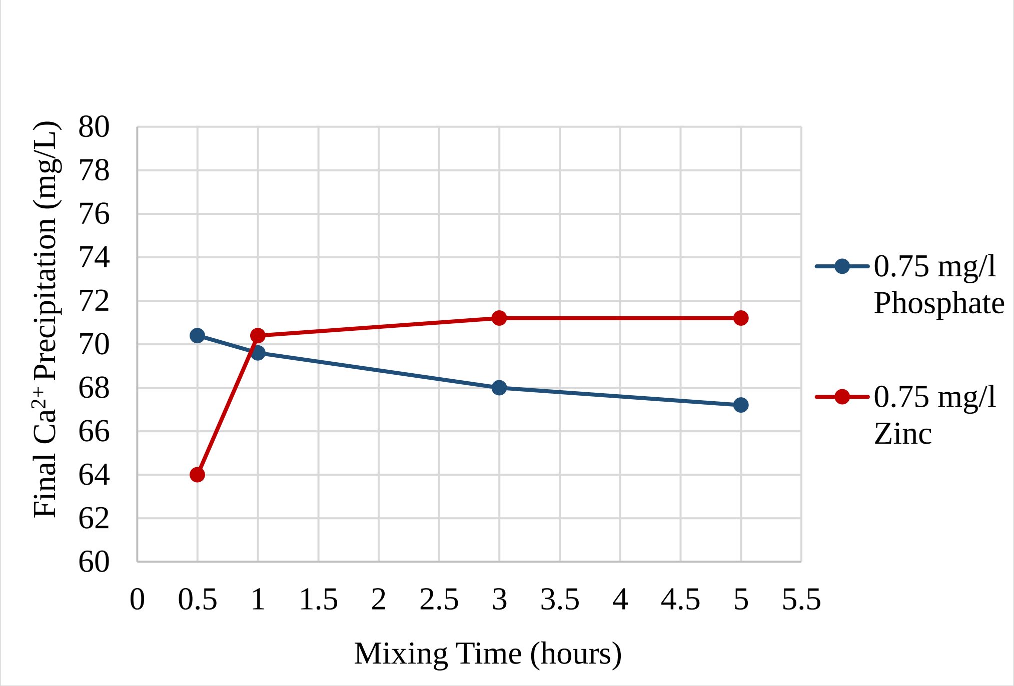


Figure 4.19(d): Final dissolved Ca^{2+} concentration as a function of mixing time for inhibitor (i.e., Zn and phosphate) concentration of 0.75 mg/L

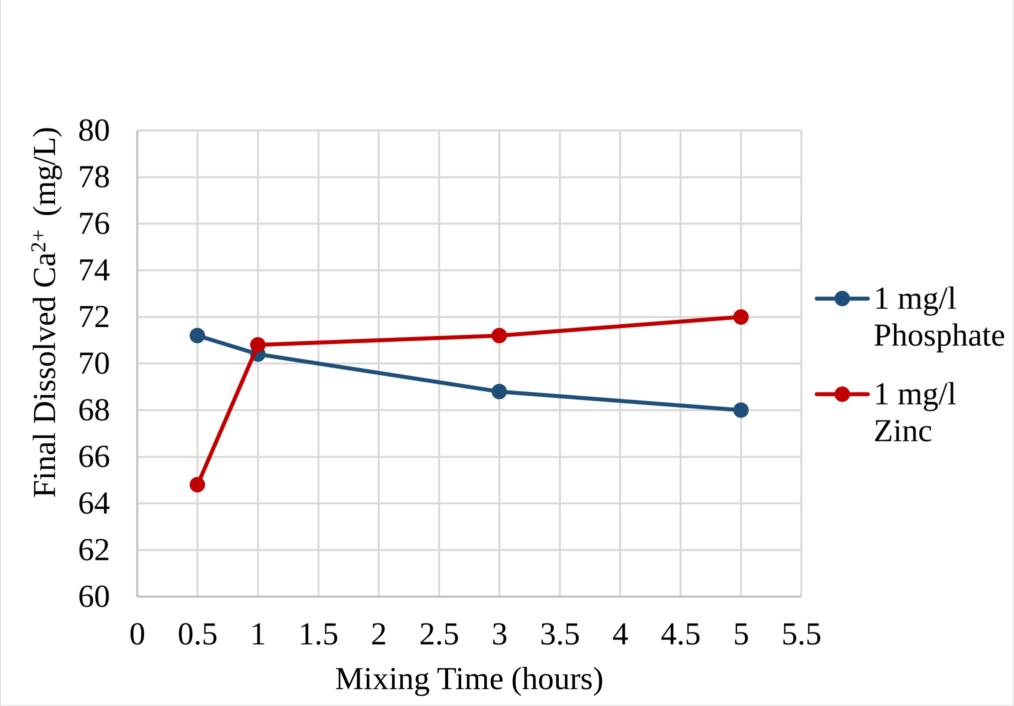


Figure 4.19(e): Final dissolved Ca^{2+} concentration as a function of mixing time for inhibitor (i.e., Zn and phosphate) concentration of 1 mg/L

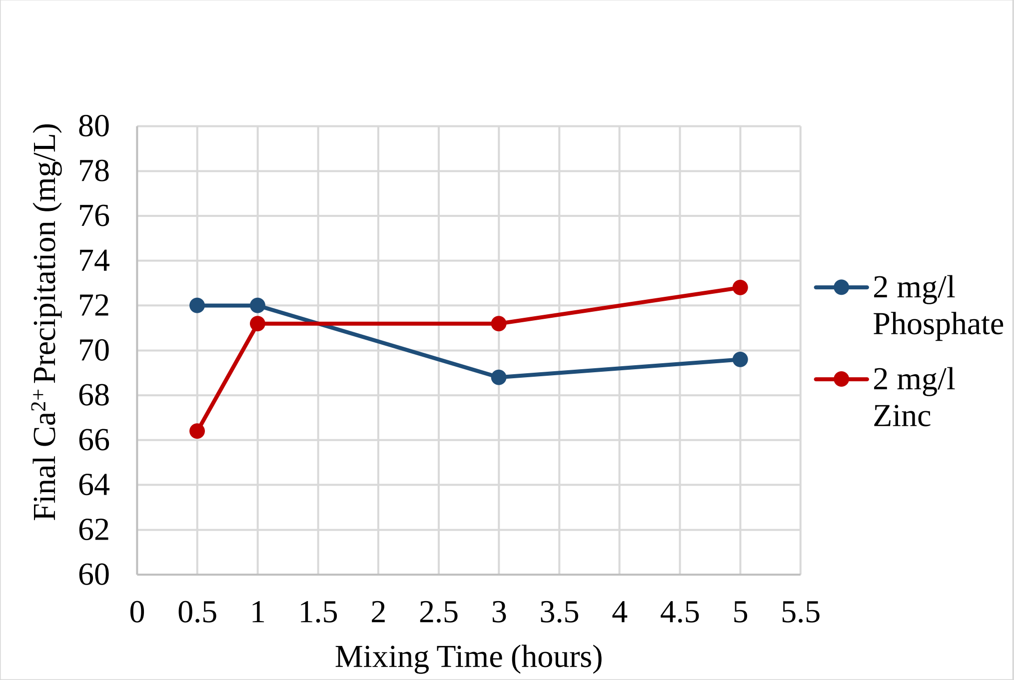


Figure 4.19(f): Final dissolved Ca^{2+} concentration as a function of mixing time for inhibitor (i.e., Zn and phosphate) concentration of 2 mg/L

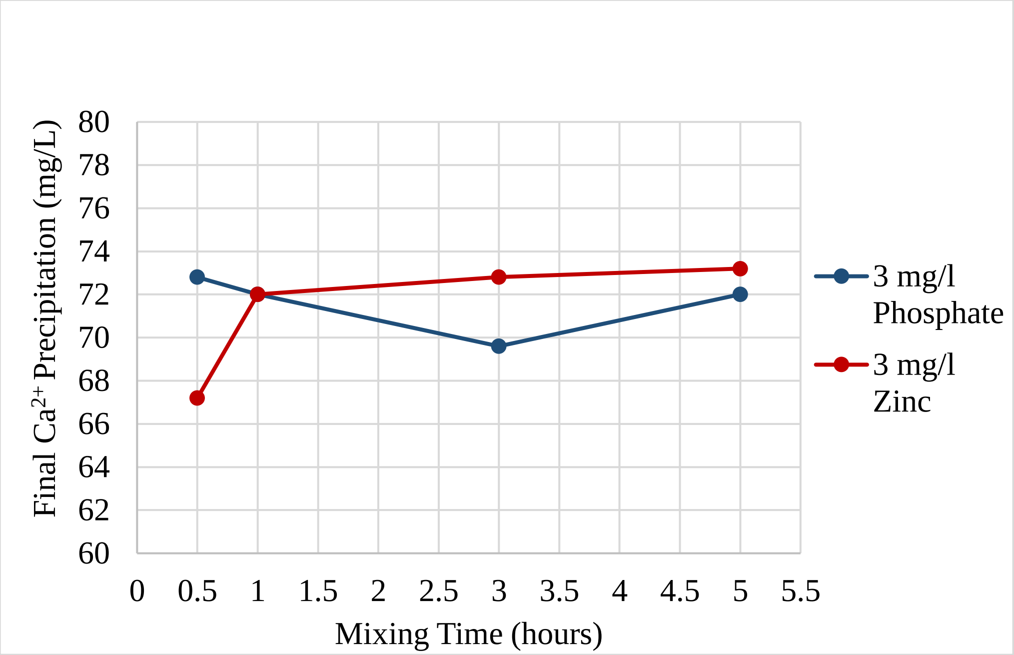


Figure 4.19(g): Final dissolved Ca^{2+} concentration as a function of mixing time for inhibitor (i.e., Zn and phosphate) concentration of 3 mg/L

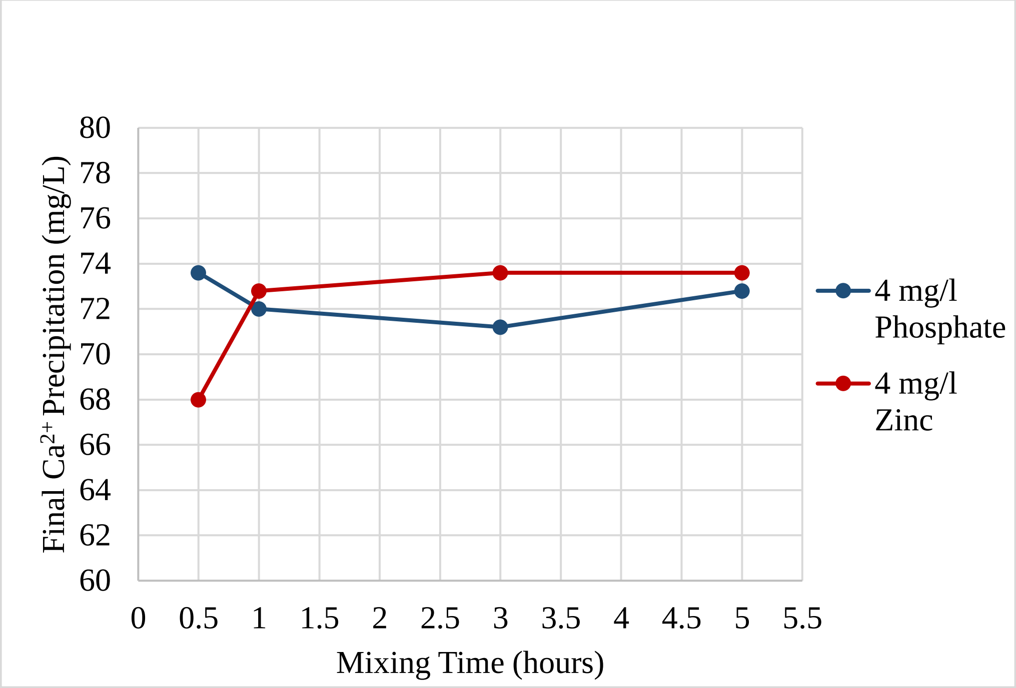


Figure 4.19(h): Final dissolved Ca^{2+} concentration as a function of mixing time for inhibitor (i.e., Zn and phosphate) concentration of 4 mg/L

4.5 Effect of Phosphate and Zn on Precipitation of $CaCO_3$(s) in Natural Groundwater

It should be noted that the natural groundwater sample used for this study had a phosphate concentration of 0.54 mg/l and a Zn concentration of 0.254 mg/l. In addition, the groundwater had a silica concentration of 66 mg/l, which has been reported to promote precipitation of $CaCO_3$(s) [9]. Thus, significant concentrations of phosphate and Zn were already present in the natural groundwater samples used in these experiments. As explained in Chapter 3, in the batch experiments carried out with this natural groundwater, additional phosphate or Zn were added to assess the effect of these inhibitors. Therefore, the results of the batch experiments would provide us the combined effects of both naturally occurring phosphate/Zn as well as the added phosphate/Zn.

4.5.1 Effect of Phosphate on Precipitation of $CaCO_3$(s) in Natural Groundwater

Table 4.15 shows the effect of added phosphate on the precipitation of $CaCO_3$(s) for the experimental conditions shown in the table. The last column of the table shows the dissolved Ca concentration for each experimental system. Table 4.15 shows that as total phosphate concentration increased from 1.54 mg/l to 4.54 mg/l, dissolved Ca concentration in fact decreased; that is, precipitation of calcium actually increased. The effect of mixing time (varying from 0.5 hr to 5 hr) on calcium concentration was not very significant. At a phosphate concentration of 1.54 mg/l, average dissolve Ca concentration was about 61.7 mg/l, while at a phosphate concentration of 4.54 mg/l, average dissolved Ca concentration was about 49.9 mg/l.

Table 4.16 shows the effect of added phosphate on the precipitation of $CaCO_3$(s) for another set of experimental conditions. It also shows that as phosphate concentration increased from 0.54 mg/l (present naturally in water) to 4.54 mg/l, dissolved Ca concentration decreased; that is precipitation of Ca increased.

Table 4.15: Results of batch experiments carried out with groundwater amended with $NaHCO_3$ and with pH adjusted at about 8.35

Experimental conditions:
Total Ca = 72.2 mg/l; Mg = 19.3 mg/l, Chloride = 75 mg/l, Total Alkalinity = 276 mg/l; Silica = 66 mg/l; Initial Phosphate = 0.54 mg/l; Initial Zn = 0.254 mg/l

Phosphate (total) (mg/l)	pH	Temp (°C)	Mixing Time (hr)	Dissolved Ca (mg/l)
1.54	8.3	28.7	0.5	63.4
	8.4	27.7	1.0	61.1
	8.3	28.5	3.0	61.1
	8.4	28.7	5.0	61.1
4.54	8.2	28.8	0.5	49.1
	8.3	28.5	1.0	50.7
	8.3	28.6	3.0	49.1
	8.4	28.0	5.0	50.6

Table 4.16: Results of batch experiments carried out with groundwater amended with $NaHCO_3$ and $CaCl_2$ solution

Experimental conditions: Total Ca = 117 mg/l; Mg = 19.3 mg/l, Total Alkalinity = 280 mg/l; Silica = 66 mg/l; Initial Chloride = 75 mg/l, Initial Phosphate = 0.54 mg/l; Initial Zn = 0.254 mg/l				
Phosphate (total) (mg/l)	pH	Temp (°C)	Mixing Time (hr)	Dissolved Ca (mg/l)
0.54 (naturally present)	7.3	28.8	0.5	117.0
	7.5	28.7	1.0	115.5
	8.1	28.5	3.0	115.5
4.54	7.4	29.0	0.5	99.5
	7.9	29.0	1.0	97.9
	8.0	28.2	3.0	96.3

These results are in contrast to the results of the batch experiments carried out in electrolyte solutions, where significant inhibition effect [i.e., inhibition of $CaCO_3$(s) precipitation] of both phosphate and Zn was observed, with increasing inhibition effect at higher phosphate/Zn concentrations. These results (in natural groundwater) show that precipitation of Ca actually increased as phosphate concentration increased. It should be noted that previous studies that reported inhibition effect of phosphate and Zn were carried out in electrolyte solutions and not in natural water/groundwater (which typically contains a range of chemical constituents).

There could be a couple of reasons for this observation:

1. Enhanced precipitation of $CaCO_3$(s) in the presence of silica (present at a concentration of 66 mg/l in groundwater), as reported by Kellermeier et al. (2013) [9].
2. Possible precipitation of Ca-PO_4 solids [in addition to $CaCO_3$(s)], as observed in the MINEQL+ model simulations.

These results therefore suggest that the inhibition effect of phosphate in natural groundwater could be governed by the possible complex effects silica [that promotes formation/precipitation of $CaCO_3(s)$] and possible precipitation of Ca-PO_4 solids (e.g., hydroxyapatite).

MINEQL+ model simulations were carried out to assess the speciation of chemical constituents in the experimental system under perfect “equilibrium condition”. The simulations were run for the following initial conditions:

$(Ca)_T$ = 72.2 mg/l = 1.805×10^{-3} M
$(Mg)_T$ = 19.3 mg/l = 7.94×10^{-4}
(Cl^-) = 75 mg/l = 2.11×10^{-3} M
pH = 8.35
Alkalinity = 276 mg/l as $CaCO_3$
$(Zn)_T$ = 0.254 mg/l = 3.88×10^{-6} M (present naturally in groundwater)
$(PO_4^{3-})_T$ = 1.54 mg/l (=1.60×10^{-5} M) and 4.54 mg/l (=4.73×10^{-6} M)

MINEQL+ model outputs show that, for the above mentioned condition (at both phosphate concentrations considered), only about 4 mg/l of total calcium remains in water in dissolved (Ca^{2+}) state; the remaining calcium (i.e. about 93%) precipitates as Calcite [$CaCO_3(s)$, about 52.4%], dolomite [$CaMg(CO_3)_2(s)$, about 40%] and Hydroxyapatite [$Ca_5(PO_4)_3(OH)(s)$ about 1.5%]. The model results show that in the presence of Mg, dolomite would also precipitate under “equilibrium” condition. Figure 4.20 shows simulated distribution of Ca species (MINEQL+ output) in water for a phosphate concentration of 4.54 mg/l (=4.73×10^{-6} M).

It is difficult to come to a conclusion about the reasons for the inability of phosphate in reducing precipitation of calcium carbonate in natural groundwater system. However, based on the experimental results, model output and information gathered from the literature (regarding effects of silica), the most likely reason appears to be possible effect of silica in enhancing precipitation of calcite (and possibly dolomite) and possible precipitation of Hydroxyapatite.

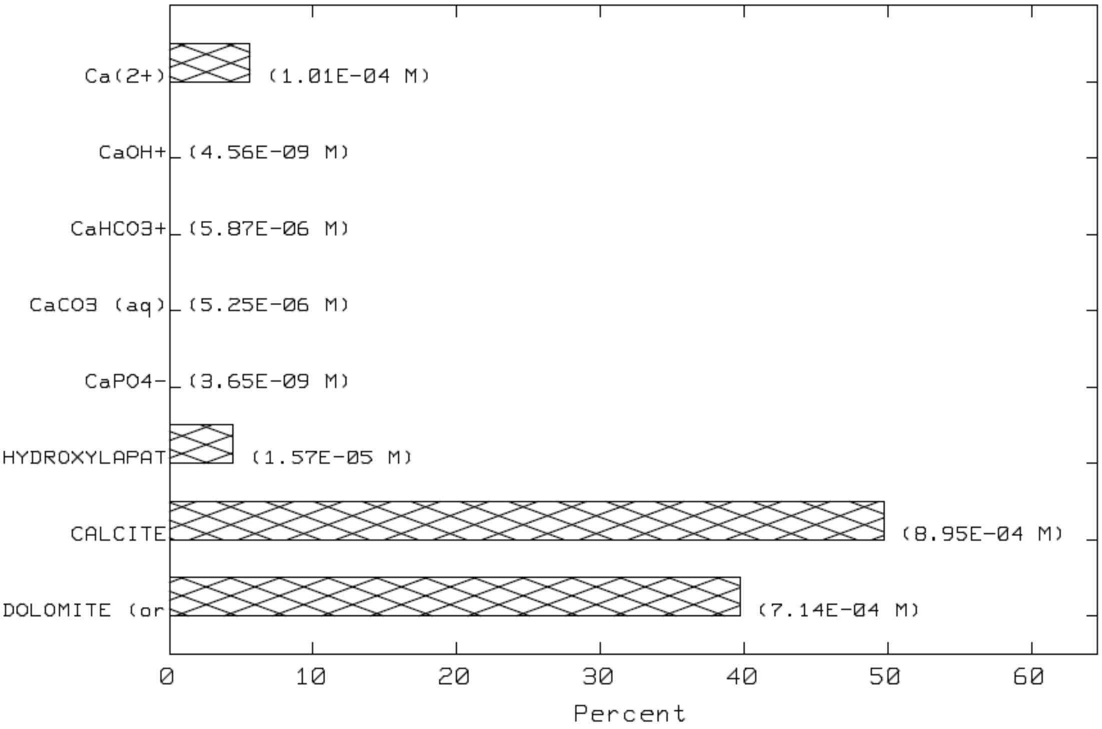


Figure 4.20: MINEQL+ output showing distribution of Ca species in the experimental groundwater system (presented above) a phosphate concentration of 4.54 mg/l (=4.73 x 10^{-6} M)

4.5.2 Effect of Zn on Precipitation of $CaCO_3$(s) in Natural Groundwater

In order to assess the effect of added Zn on precipitation of $CaCO_3$(s), three sets of experiments were carried out. Table 4.10 shows the effect of added Zn on the precipitation of $CaCO_3$(s) for one set of experiments; the experimental conditions noted in the table. The last column of the table shows the dissolved Ca concentration for each experimental system. Table 4.17 shows that as total Zn concentration increased from 1.254 mg/l to 3.254 mg/l, dissolved Ca concentration in fact decreased; that is, precipitation of calcium actually increased; the effect of mixing time (varying from 0.5 hr to 5 hr) on calcium concentration was not very significant. At a Zn concentration of 1.254 mg/l, average dissolve Ca concentration was about 63.5 mg/l, while at a Zn concentration of 3.254 mg/l, average dissolved Ca concentration was about 53.9 mg/l.

Table 4.18 shows the effect of added Zn on the precipitation of $CaCO_3$(s) for another set of experiments. It also shows that as Zn concentration increased from 0.254 mg/l (present naturally in water) to 3.254 mg/l, dissolved Ca concentration decreased (by about 10% on an average); that is precipitation of Ca increased.

Table 4.19 shows effect of added Zn on precipitation of $CaCO_3$(s) from the third set of experiments, where the pH of groundwater was increased to about 8.0 (without amending the concentrations of Ca and carbonates). It also shows slight decrease of dissolved Ca concentration with increasing (from zero to 1.254 mg/l) Zn concentration in water.

Table 4.17: Results of batch experiments carried out with groundwater amended with $NaHCO_3$ and with pH adjusted at about 8.35

Experimental conditions:

Total Ca = 72.2 mg/l; Mg = 19.3 mg/l, Chloride = 75 mg/l, Total Alkalinity = 276 mg/l; Silica = 66 mg/l; Initial Phosphate = 0.54 mg/l; Initial Zn = 0.254 mg/l

Zinc (total) (mg/l)	pH	Temp (°C)	Mixing Time (hr)	Dissolved Ca (mg/l)
1.254	8.1	28.5	0.5	62.7
	8.2	28.2	1.0	63.5
	8.6	28.7	3.0	63.5
	8.6	28.8	5.0	64.3
3.254	8.1	28.5	0.5	53.9
	8.2	27.9	1.0	55.5
	8.4	28.8	3.0	53.8
	8.5	28.4	5.0	52.3

Table 4.18: Results of batch experiments carried out with groundwater amended with $NaHCO_3$ and $CaCl_2$ solution

Experimental conditions:

Total Ca = 117 mg/l; Mg = 19.3 mg/l, Total Alkalinity = 280 mg/l; Silica = 66 mg/l; Initial Chloride = 75 mg/l, Initial Phosphate = 0.54 mg/l; Initial Zn = 0.254 mg/l

Zinc (total) (mg/l)	pH	Temp (°C)	Mixing Time (hr)	Dissolved Ca (mg/l)
0.254 (naturally present)	7.3	28.8	0.5	117.0
	7.5	28.7	1.0	115.5
	8.1	28.5	3.0	115.5
3.254	7.3	28.9	0.5	101.1
	7.5	28.9	1.0	104.3
	7.8	28.4	3.0	105.9

Table 4.19: Results of batch experiments carried out with groundwater after adjusting its pH to about 8 by addition of dilute NaOH solution

Experimental conditions:

pH of groundwater raised to about 8.0 by addition of NaOH; Total Ca = 72.2 mg/l; Mg = 19.3 mg/l, Total Alkalinity = 218 mg/l; Silica = 66 mg/l; Initial Chloride = 75 mg/l, Initial Phosphate = 0.54 mg/l; Initial Zn = 0.254 mg/l

Zinc (total) (mg/l)	pH	Temp (°C)	Mixing Time (hr)	Dissolved Ca (mg/l)
0.254 (naturally present)	7.89	24.8	0.5	72.0
	8.11	25.0	1.0	72.1
0.504	8.02	25.1	0.5	70.7
	8.31	24.8	1.0	69.9
1.254	8.15	24.8	0.5	69.9
	8.23	24.9	1.0	69.1

As observed for phosphate, these results with Zn are in contrast to the results of the batch experiments carried out in electrolyte solutions. These results (in natural groundwater) suggest that precipitation of Ca could increase in the presence of Zn. As noted above, all previous studies that reported inhibition effect of phosphate and Zn were carried out in electrolyte solutions and not in natural water/groundwater (which typically contains a range of chemical constituents).

There could be a couple of reasons for this observation:

(1) Enhanced precipitation of $CaCO_3(s)$ in the presence of silica (present at a concentration of 66 mg/l in groundwater), as reported by Kellermeier et al. (2013).
(2) Possible precipitation of Ca-PO_4 solids [in the presence of 0.54 mg/l phosphate in natural groundwater], as observed in the MINEQL+ model simulations.

These results therefore suggest that the inhibition effect of Zn in natural groundwater could be governed by the possible complex effects silica [that promotes formation/precipitation of $CaCO_3(s)$] and possible precipitation of Ca-PO_4 solids (e.g., hydroxyapatite).

MINEQL+ model simulations were carried out to assess the speciation of chemical constituents in the experimental system under perfect “equilibrium condition”. The simulations were run for the following initial conditions:

$(Ca)_T$ = 72.2 mg/l = 1.805×10^{-3} M
$(Mg)_T$ = 19.3 mg/l = 7.94×10^{-4}
(Cl^-) = 75 mg/l = 2.11×10^{-3} M
pH = 8.35
Alkalinity = 276 mg/l as $CaCO_3$
$(PO_4^{3-})_T$ = 0.54 mg/l = 5.625×10^{-6} M (present naturally in groundwater)
$(Zn)_T$ = 1.254 mg/l (= 1.92×10^{-5} M) and 3.254 mg/l (= 4.98×10^{-5} M)

The MINEQL+ model outputs were similar to those found for the simulations in the presence of added phosphate. The model outputs show that, irrespective of the Zn concentrations considered, majority of Ca precipitates as calcite and dolomite under “equilibrium”; only about 4 mg/l of Ca remains in dissolved state (Ca^{2+}). Unlike the simulations carried out for the experimental systems in electrolyte (NaCl) solution, $ZnCO_3(s)$ did not precipitate in the groundwater systems, which is due to the preferential precipitation of dolomite (in the presence of Mg).

Therefore, as noted above, the most likely reason for the inability of Zn in reducing precipitation of Ca appears to be possible effect of silica in enhancing precipitation of calcite, and possibly dolomite.

4.6 Possible Application of Inhibitors in the Context of Bangladesh

It should be noted that all previous studies which reported inhibition effects of phosphate and Zn in the precipitation of calcium carbonates reached their conclusion based on experiments carried out in electrolyte systems (consisting of Na^+ or K^+, Cl^- and/or NO_3^-, Ca, carbonates, phosphates or Zn). This study took those studies one step forward through detailed (experimental and model) analysis of the effect of inhibitor (phosphate or Zn) concentration and mixing/equilibration time. Also, the comparison of the inhibition effect between these two inhibitors in electrolyte system was analyzed. In NaCl electrolyte solution (in deionized water), for a particular mixing time, concentration of precipitated Ca decreases as phosphate or zinc inhibitor concentration increases. The effectiveness of phosphate inhibitor was found out to be more pronounced at shorter duration of mixing, while zinc proved to be more effective at longer duration of mixing.

This study also assessed the ability of these inhibitors in natural groundwater system, and concluded that the ability of these inhibitors in natural groundwater system would be limited by the complex interactions among the diverse ions/chemical constituents present in water; most notably by the possible effect of silica (as reported in the literature) on precipitation of calcium carbonates, and possible formation of other Ca-Mg and Ca-PO_4 solids.

Therefore, addition of phosphate or Zn as inhibitors is unlikely to result in inhibition of calcium carbonate precipitation in the groundwater treatment plant (and distribution system). However, the complex interactions among the inhibitors (i.e., Zn and phosphate) and the some of the constituents of groundwater need to be studied in detail (through experimental and modeling studies) in order to reach a conclusion regarding the effects of these inhibitors on calcium carbonate precipitation.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 General

The overall objective of this research is to assess the effectiveness of phosphate and zinc as scale inhibitor in delaying precipitation $CaCO_3$ in water containing high concentrations of calcium and carbonate. This work involved laboratory batch experiments in electrolyte (NaCl) solution containing calcium chloride and sodium bicarbonate. Inhibitor phosphate and zinc were added separately as potassium dihydrogen phosphate and zinc chloride to the solutions, respectively. Similar batch experiments were also carried out with natural groundwater to assess their inhibition capacity in natural groundwater. In addition, behavior of the experimental systems under equilibrium condition was simulated using MINEQL+ chemical equilibrium model. This chapter presents the major findings of this research and also includes recommendations that would be helpful for future research works.

5.2 Conclusion

The major conclusions that have been reached from the present study are as follows:

1) In NaCl electrolyte solution, precipitation of $CaCO_3$ decreases as concentration of the inhibitor – Phosphate or Zinc– increases. For example, estimated precipitation of calcium carbonate decreased from about 10.2 mg/l in the absence of phosphate to almost zero in the presence of 5 mg/l of phosphate; while it decreased from about 14.2 mg/l in the absence of Zn to almost negligible in the presence of 4 mg/l of Zn.
2) In the electrolyte solution, the precipitation of $CaCO_3$ appears to decrease rapidly (with increase in phosphate/Zn concentration) up to phosphate or Zn concentration of about 1.0 mg/l, and then the decrease of $CaCO_3$ precipitation appears to slow down (with further increase of phosphate/Zn concentration).
3) Equilibrium model simulations (with MINEQL+) suggest that at higher phosphate concentrations, phosphate might precipitate as Ca-PO_4 solids (e.g., hydroxyapatite),

thereby reducing the availability of orthophosphate (which is apparently responsible for its inhibition effect).

4) Equilibrium model simulations (with MINEQL+) suggest that at higher Zn concentrations (exceeding about 1 mg/l), Zn might precipitate as $ZnCO_3$(s), thereby reducing the availability of Zn^{2+} (which is apparently responsible for its inhibition effect).
5) In electrolyte solution, precipitation of Ca is likely to be significant even in the presence of low concentration of the inhibitors, if the degree of super-saturation is high.
6) In electrolyte solution, the inhibition effect of phosphate appears to diminish to some extent with time, while in case of Zn, the inhibition effect appears to become stronger with time.
7) In electrolyte solution, the inhibition effect of phosphate is higher than that of Zn for shorter mixing time; but for longer period of mixing time, Zn is more effective in reducing precipitation of $CaCO_3$.
8) In natural groundwater, neither phosphate nor Zn could reduce the precipitation of $CaCO_3$(s); in fact, precipitation slightly increased.
9) The inhibitory effect of phosphate and Zn, as reported in the literature (based on experiments in electrolyte solution), does not appear to be applicable for natural groundwater systems containing silica and a range of other dissolved constituents.

5.3 Recommendations

The following topics can be suggested for future studies:

1) In this study, in batch experiments in NaCl electrolyte solution, effect of phosphate and Zn was evaluated. Studies are needed to evaluate the effect of silica, in particular, because it is likely to enhance the precipitation of calcium carbonate.

2) In batch experiments with electrolyte solution, possible precipitation Ca-PO_4 solids and $ZnCO_3$(s) should be assessed through careful measurements of dissolve phosphate and Zn concentrations (in addition to measurement of Ca concentration) in batch experiments.

3) After evaluation of the possible effect of silica on precipitation of calcium carbonate, additional studies should be carried out to better assess the combined effect of these constituents on the precipitation of calcium carbonates.

Reference

[1] Belarbi, Z., Gamby, J., Makhloufi, L., Sotta, B., and Tribollet, B, "Inhibition of calcium carbonate precipitation by aqueous extract of Paronychia argentea," J. of Cryst. Growth, vol. 386, pp. 208-214, 2014.

[2] Matty, J. M., and Tomson, M. B., "Effect of multiple precipitation inhibitors on calcium carbonate nucleation," Appl. Geochemistry, vol. 3, pp. 549-556, 1988.

[3] Amjad, Z. "Effect of precipitation inhibitors on calcium phosphate scale formation," Canadian J. Chem., vol. 67, pp. 850-856, 1989.

[4] Baylis, J. R., "Treatment of water to prevent corrosion," J. Am. Water Works Assoc., vol. 29, pp. 220-234, 1935.

[5] Garrett-Price, B. A., Smith, S. A., Watts, R. L., and Knudsen, J. G. (1985) *Fouling of heat exchangers: Characteristics, costs, prevention, control and removal*. Noyes Publications, New Jersey.

[6] Richards, C. S., *Calcium Carbonate Formation in Water Distribution Systems and Autogenous Repair of Leaks by Inert Particle Clogging,* Master of Science Thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA, 2016.

[7] BRTC, BUET (2019), Assessment of Raw Water Quality, Identification of Scaling Problem, Propose Modification of Treatment Processes and Preliminary Design of Treatment Processes at Meherpur Paurashava, Report prepared for the Local Government Engineering Department (LGED), Bureau of Research Testing and Consultation, BUET, November, 2019.

[8] Crabtree, M., Eslinger, D., Fletcher, P., Miller, M., and Johnson, A., "Fighting scale: removal and prevention," Oilfield Review, vol. 11, pp. 30-45, 1999.

[9] Kellermeier, M., Glaab, F., Klein, R., Melero-Garcia, E., Kunz, W., and García-Ruiz, J. M., "The effect of silica on polymorphic precipitation of calcium carbonate: an on-line energy-dispersive X-ray diffraction (EDXRD) study," Nanoscale, vol. 5, pp. 7054-7065, 2013.

[10] Wada, N., Yamashita, K., and Umegaki, T., "Effects of divalent cations upon nucleation, growth and transformation of calcium carbonate polymorphs under conditions of double diffusion," J. Cryst. Growth, vol. 148, pp. 297-304, 1995.

[11] Ghizellaoui, S., and Euvrard, M., "Assessing the effect of zinc on the crystallization of calcium carbonate. Desalination," vol. 220, pp. 394-402, 2008.

[12] Lin, Y. and Singer, P.C., "Inhibition of calcite precipitation by orthophosphate: speciation and thermodynamic considerations," Geochimicha et Cosmochimica Acta, vol. 70, pp. 2530-2539, 2006.

[13] Yang, Q., Liu, Y., Gu, A., Ding, J., and Shen, Z., “Investigation of calcium carbonate scaling inhibition and scale morphology by AFM,” J. Colloid Interface Sci., vol. 240, pp. 608-621, 2001.

[14] Lin, Y. and Singer, P.C., “Effect of Mg^{2+} on the kinetics of calcite crystal growth,” J. Cryst. Growth, vol. 312, pp. 136-140, 2009.

[15] Velloso Alves de Souza, A., Rosário, F., and Cajaiba, J., “Evaluation of Calcium Carbonate Inhibitors Using Sintered Metal Filter in a Pressurized Dynamic System,” Materials, vol. 12, p. 1849, 2019.

[16] Brooks, R., Clark, L. M., and Thurston, E. F., “Calcium carbonate and its hydrates,” Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences, vol. 243, pp. 145-167, 1950.

[17] Plummer, L. N., and Busenberg, E., “The solubilities of calcite, aragonite and vaterite in CO_2-H_2O solutions between 0° and 90° C, and an evaluation of the aqueous model for the system $CaCO_3$-CO_2-H_2O. Geochimica et cosmochimica acta, vol. 46, pp. 1011-1040, 1982.

[18] Brecevic L. and Nielsen A. E. (1989). Solubility of amorphous calcium carbonate. Journal of Crystal Growth, 98(3), 504-510

[19] Kralj, D., and Brečević, L., “Dissolution kinetics and solubility of calcium carbonate monohydrate,” Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 96, pp. 287-293, 1995.

[20] Kabasci, S., Althaus, W., and Weinspach, P. M., “Batch-Precipitation of Calcium-Carbonate from Highly Supersaturated Solutions,” Chem. Engg. Research & design, vol. 74, pp. 765-772, 1996.

[21] Ogino, T., Suzuki, T., and Sawada, K., “The rate and mechanism of polymorphic transformation of calcium carbonate in water,” J of Cryst. Growth, vol. 100, pp. 159-167, 1990.

[22] Perić, J., Vučak, M., Krstulović, R., Brečević, L., and Kralj, D., “Phase transformation of calcium carbonate polymorphs,” Thermochimica Acta, vol. 277, pp. 175-186, 1996.

[23] Sawada, K., “The mechanisms of crystallization and transformation of calcium carbonates,” Pure and Appl. Chem., vol. 69, pp. 921-928, 1997.

[24] Rybacki K. S., *Calcium Carbonate Precipitation Mechanisms and Geochemical analysis of Particulate Material found within the waters of Maramec Spring, St. James, Missouri*, M. Sc. Engg. Thesis, Department of Geology & Geophysics, Missouri University of Science and Technology, 2010.

[25] Dove, P. M., and Hochella Jr, M. F., “Calcite precipitation mechanisms and inhibition by orthophosphate: In situ observations by Scanning Force Microscopy,” Geochimica et cosmochimica acta, vol. 57, pp. 705-714, 1993.

[26] Dreybrodt, W., Eisenlohr, L., Madry, B., and Ringer, S., “Precipitation kinetics of calcite in the system $CaCO_3$-H_2O-CO_2: The conversion to CO_2 by the slow process $H^+ + HCO_3^- \rightarrow CO_2 + H_2O$ as a rate limiting step,” Geochimica et Cosmochimica Acta, vol. 61, pp. 3897-3904, 1997.

[27] Wilson, J.L. (1975) *Carbonate Facies in Geologic History*, Springer-Verlag, Berlin.

[28] Lebron, I., and Suarez, D. L., “Calcite nucleation and precipitation kinetics as affected by dissolved organic matter at 25ºC and pH> 7.5,” Geochimica et Cosmochimica Acta, vol. 60, pp. 2765-2776, 1996.

[29] Reddy, M. M., and Nancollas, G. H., “The crystallization of calcium carbonate: I. Isotopic exchange and kinetics,” J. Colloid Interface Science, vol. 36, pp. 166-172, 1971.

[30] Lakshtanov, L. Z., and Stipp, S. L. S., “Interaction between dissolved silica and calcium carbonate: 1. Spontaneous precipitation of calcium carbonate in the presence of dissolved silica”, Geochimica et Cosmochimica Acta, vol. 74, pp. 2655-2664, 2010.

[31] Zhang, Y., and Grattoni, C. A., “Comment on “Precipitation kinetics of calcite in the system $CaCO_3$-H_2O-CO_2: the conversion to CO_2 by the slow process $H^+ + HCO_3^- \rightarrow CO_2 + H_2O$ as a rate limiting step” by W. Dreybrodt, L. Eisenlohr, B. Madry, and S. Ringer,” Geochimica et cosmochimica acta, vol. 62, pp. 3789-3790, 1998.

[32] Kamkha, M. A., Sibiryakov, P. B., and Bizyaev, V. L., “Effect of the pH on the kinetics of mass crystallization of calcium-carbonate,” Kinetics and Catalysis, vol. 30, pp. 62-67, 1989.

[33] Gómez-Morales, J., Torrent-Burgués, J., López-Macipe, A., and Rodríguez-Clemente, R., “Precipitation of calcium carbonate from solutions with varying Ca2+ carbonate ratios,” J. Cryst. Growth, vol. 166, pp. 1020-1026, 1996.

[34] Teng, H. H., Dove, P. M., and De Yoreo, J. J., “Kinetics of calcite growth: surface processes and relationships to macroscopic rate laws,” Geochimica et Cosmochimica Acta, vol. 64, pp. 2255-2266, 2000.

[35] Dickinson, S. R., Henderson, G. E., and McGrath, K. M., “Controlling the kinetic versus thermodynamic crystallisation of calcium carbonate,” J. Cryst. Growth, vol. 244, pp. 369-378, 2002.

[36] Karbonatsystem Meerwasser de.svg, 2010, Carbonate system of seawater, https://commons.wikimedia.org/wiki/File:Carbonate_system_of_seawater.svg#metadata [Last access on 19 Nov. 2020].

[37] Reddy, M. M., and Nancollas, G. H., “The crystallization of calcium carbonate: IV. The effect of magnesium, strontium and sulfate ions,” J. Cryst. Growth, vol. 35(1), pp. 33-38, 1976.

[38] Swinney, L. D., Stevens, J. D., and Peters, R. W., “Calcium carbonate crystallization kinetics,” Industrial & Engg. Chem. Fund., vol. 21, pp. 31-36, 1982.

[39] Goodarz-nia, I., and Motamedi, M., “Kinetics of calcium carbonate crystallization from aqueous solutions,” J. Cryst. Growth, vol. 49, pp. 125-131, 1980.

[40] Nancollas, G. H., and Reddy, M. M., “The crystallization of calcium carbonate. II. Calcite growth mechanism,” J. Colloid Interface Sci., vol. 37, pp. 824-830, 1971.

[41] Reddy, M. M., and Gaillard, W. D., “Kinetics of calcium carbonate (calcite)-seeded crystallization: Influence of solid/solution ratio on the reaction rate constant,” J. Colloid Interface Sci., vol. 80, pp. 171-178, 1981.

[42] Reddy, M. M., and Nancollas, G. H., “Calcite crystal growth inhibition by phosphonates,” Desalination, vol. 12, pp. 61-73, 1973.

[43] Nancollas, G. H., “The growth of crystals in solution,” Adv. Colloid Interface Sci., vol. 10, pp. 215-252, 1979.

[44] Söhnel, O., and Mullin, J. W., “Precipitation of calcium carbonate,” J. Cryst. Growth, vol. 60, pp. 239-250, 1982.

[45] Gebauer, D., Völkel, A., and Cölfen, H., “Stable prenucleation calcium carbonate clusters,” Science, vol. 322, pp. 1819-1822, 2008.

[46] Amor, M. B., Zgolli, D., Tlili, M. M., and Manzola, A. S., “Influence of water hardness, substrate nature and temperature on heterogeneous calcium carbonate nucleation,” Desalination, vol. 166, pp. 79-84, 2004.

[47] Gal, J. Y., Fovet, Y., and Gache, N., “Mechanisms of scale formation and carbon dioxide partial pressure influence. Part I. Elaboration of an experimental method and a scaling model,” Water research, vol. 36, pp. 755-763, 2002.

[48] Chong, T. H., and Sheikholeslami, R., “Thermodynamics and kinetics for mixed calcium carbonate and calcium sulfate precipitation,” Chem Engg. Sci., vol. 56, pp. 5391-5400, 2001.

[49] Logsdon, G.S., Hess, A.F., Chipps, M.J., and Rachwal, A.J., “Filter Maintenance and Operations Guidance Manual,” Denver, CO: AWWA, 2002.

[50] Gwon, E. M., Yu, M. J., Oh, H. K., and Ylee, Y. H., “Fouling characteristics of NF and RO operated for removal of dissolved matter from groundwater,” Water Research, vol. 37, pp. 2989-2997, 2003.

[51] Bremere, I., Kennedy, M., Michel, P., van Emmerik, R., Witkamp, G. J., and Schippers, J., "Controlling scaling in membrane filtration systems using a desupersaturation unit," Desalination, vol. 124, pp. 51-62, 1999.

[52] Seneviratne, M., *A Practical Approach to Water Conservation for Commercial and Industrial Facilities*. Elsevier, 2007.

[53] Brazeau, R. H., and Edwards, M. A., "A review of the sustainability of residential hot water infrastructure: Public health, environmental impacts, and consumer drivers," College Publishing, vol. 6, pp. 77-95, 2011.

[54] Water Quality Research Foundation (WQRF) (2011). Softened Water Benefits Study (Energy and Detergent Savings). Lisle, IL: Water Quality Association.

[55] Houska, C. (2007). Deicing salt – recognizing the corrosion threat. *International Molybdenum Association, Pittsburgh, TMR Consulting*.

[56] Dobersek, D., and Goricanec, D., "Influence of water scale on thermal flow losses of domestic appliances," Int. J. Math. Models and Methods Appl. Sci., vol. 1, pp. 55-61, 2007.

[57] Krappe, J.M. (1940). "*Scale Formation in Water Heaters"*, Purdue University Lafayette, IN, USA.

[58] Roy, S. and Edwards, M.E., "Role of water hardness precipitation and flashing cavitation in erosion corrosion of copper in potable water systems," in *134th AWWA Annual Conference and Exposition (ACE),* Anaheim, CA, June 2015, pp. 7-8, 2015.

[59] Anderson, P.W. and Faust, S.D., "Impact of drought on quality in a New Jersey water supply system," Water Resources Bulletin (American Water Works Association), vol. 8, pp. 750-760, 1972.

[60] Mosley, L.M., "Drought impacts on the water quality of freshwater systems; review and integration," Earth-Sci. Rev., vol. 140, pp. 203-214, 2015.

[61] Freeman, C., Evans, C.D., and Monteith, D.T., "Export of organic carbon from peat soils," Nature, vol. 412, p. 785, 2001.

[62] Mullin, J.W. (2001). *Nucleation. In: Crystallization*. 4th Ed., Butterworth Heinemann, Oxford, UK.

[63] Brezonik, P.L. and Arnold, W.A. *Water Chemistry: An Introduction to the Chemistry of Natural and Engineering Aquatic Systems*. Oxford University Press, New York, NY, 2011.

[64] Xyla, A.G., Giannimaras, E.K., and Koutsoukos, P.G., "The precipitation of calcium carbonate in aqueous solutions," Colloids and Surfaces, vol. 53, pp. 241-255, 1991.

[65] Lioliou, M.G., Paraskeva, C.A., Koutsoukos, P.G., and Payatakes, A.C., “Heterogeneous nucleation and growth of calcium carbonate on calcite and quartz,” J. Colloid and Interface Sci., vol. 308, pp. 421-428, 2007.

[66] Gebauer, D., Kellermeier, M., Gale, J.D., Bergström, L., and Cölfen, H., “Pre-nucleation clusters as solute precursors in crystallisation. Chemical Society Reviews, vol. 43, pp. 2348-2371, 2014.

[67] Lam, R.S.K., Charnock, J.M., Lennie, A., and Meldrum, F.C., “Synthesis-dependent structural variations in amorphous calcium carbonate,” Cryst. Eng. Comm., vol. 9, pp. 1226-1236, 2007.

[68] Ng, J.D., Lorber, B., Witz, J., Théobald-Dietrich, A., Kern, D., and Giegé, R. “The crystallization of biological macromolecules from precipitates: evidence for Ostwald ripening,” J. Cryst. Growth, vol. 168, pp. 50-62, 1996.

[69] Wolf, S.E., Leiterer, J., Kappl, M., Emmerling, F., and Tremel, W., “Early homogeneous amorphous precursor stages of calcium carbonate and subsequent crystal growth in levitated droplets,” J. Am. Chem. Soc., vol. 130, pp.12342-12347, 2008.

[70] Ogino, T., Suzuki, T., and Sawada, K., “The formation and transformation mechanism of calcium carbonate in water,” Geochimica et Cosmochimica Acta, vol. 51, pp. 2757-2767, 1987.

[71] Keysar, S., Semiat, R., Hasson, D., and Yahalom, J., “Effect of surface roughness on the morphology of calcite crystallization in mild steel,” J. Colloid Interface Sci., vol. 162, pp. 311-319, 1994.

[72] Wu, Z., Davidson, J.H., and Francis, L.F., “Effect of water chemistry on calcium carbonate deposition on metal and polymer surfaces,” J. Colloid Interface Sci., vol. 343, pp. 176-187, 2010.

[73] Cheong, W.C., Gaskell, P.H., and Neville, A., “Substrate effect on surface adhesion/crystallisation of calcium carbonate,” J. Cryst. Growth, vol. 363, pp. 7-21, 2013.

[74] MacAdam, J. and Parsons, S.A., “Calcium carbonate scale formation and control,” Rev. Env. Sci. Bio/Tech., vol. 3, pp. 159-169, 2004.

[75] Githens, R.E., Minor, W.R., and Tomsic, V.J., “Flexible-tube heat exchangers,” Chem. Engg. Prog., vol. 61, p. 55, 1965.

[76] Wu, Z., Francis, L.F., and Davidson, J.H., “Scale formation on polypropylene and copper tubes in mildly supersaturated tap water,” Solar Energy, vol. 83, pp. 636-645, 2009.

[77] Reddy, M.M. and Wang, K.K., “Crystallization of calcium carbonate in the presence of metal ions: I. Inhibition by magnesium ion at pH 8.8 and 25 °C,” J. Cryst. Growth, vol. 50, pp. 470-480, 1980.

[78] Lin, Y. and Singer, P.C., “Inhibition of calcite crystal growth by polyphosphates,” Water Research, vol. 39, pp. 4835-4843, 2005.

[79] Lin, Y., Singer, P.C., and Aiken, G.R., “Inhibition of calcite precipitation by natural organic material: kinetics, mechanism, and thermodynamics,” Env. Sci. & Tech., vol. 39, pp. 6420-6428, 2005.

[80] Hoch, A.R., Reddy, M.M., and Aiken, G.R., “Calcite crystal growth inhibition by humic substances with emphasis on hydrophobic acids from the Florida Everglades,” Geochimica et Cosmochimica Acta, vol. 64, pp. 61-72, 2000.

[81] Hatch, G.B., “Control of calcium carbonate deposition for corrosion inhibition,” United States Patent no. US2299748, 1942.

[82] Primus, N.S. and Hunhoff, R., “Method for Lining Pipes with Calcite”, United States Patent no. US3640759, 1972.

[83] Clarkson, J.R., Price, T.J., and Adams, C.J., “Role of metastable phases in the spontaneous precipitation of calcium carbonate”, J. Chem. Soc., Faraday Transactions, vol. 88, pp. 243-249, 1992.

[84] Morse, J.W., Arvidson, R.S., and Lüttge, A., “Calcium carbonate formation and dissolution. Chemical Reviews, vol. 107, pp. 342-381, 2007.

[85] American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE). Legionellosis: Risk Management for Building Water Systems. Atlanta, GA: ANSI/ASHRAE, 2015.

Appendix

Table 1: Findings of experiment with 75 mg/L Ca^{2+} Test for 30 minutes mixing time with PO_4^{3-} inhibitor

Ca^{2+} Test (75 mg/L)						
Mixing Time 30 minutes (Alkalinity = 200, Target Ω = 11)						
Sample No.	pH	Temperature (°celsius)	PO_4^{3-} Conc. (mg/L)	$CaCO_3$ 1/2 Hardness (mg/L)	Final Dissolved Ca^{2+} (mg/L)	Final Precipitation (mg/L)
1	8.04	24.9	0	81	64.8	10.2
2	8.08	24.7	0.1	83	66.4	8.6
3	8.08	24.6	0.25	84	67.2	7.8
4	8.02	24.5	0.5	86	68.8	6.2
5	8.07	25	0.75	88	70.4	4.6
6	8.09	24.8	1	89	71.2	3.8
7	8.11	24.5	2	90	72	3
8	8.27	24.5	3	91	72.8	2.2
9	7.89	24.8	4	92	73.6	1.4
10	7.94	24.7	5	92	75	0
Average	8.06	24.7				

Table 2: Calculation of Saturation Index of 75 mg/L Ca^{2+} Test for 30 minutes mixing time with PO_4^{3-} inhibitor

Avg. pH	**Temp. (°C)**	**Initial Ca^{2+} (M)**	**kw**	**kA_2**	**CO_3^{2-} as $CaCO_3$**	**CO_3^{2-} as mg/L as CO_3^{2-}**	**CO_3^{2-} (M)**	**Q**	**log(K_{sp})**	**Saturation Index**
8.06	24.7	0.001875	9.89414 E-15	4.65243 E-11	2.108691737	1.265215042	2.10869 E-05	3.9538 E-08	-8.477302798	11.87

Table 3: Findings of experiment with 100 mg/L Ca^{2+} Test for 30 minutes mixing time with PO_4^{3-} inhibitor

Ca^{2+} Test (100 mg/L)						
Mixing Time 30 minutes (Alkalinity = 200, Target Ω = 15)						
Sample No.	pH	Temperature (°celsius)	PO_4^{3-} Conc. (mg/L)	$CaCO_3$ 1/2 Hardness	Final Dissolved Ca^{2+} (mg/L)	Final Precipitation (mg/L)
1	8.41	22.8	0	108	86.4	13.6
2	8.38	22.8	0.1	110	88	12
3	8.45	22.8	0.25	111	88.8	11.2
4	8.43	22.7	0.5	112	89.6	10.4
5	8.34	22.6	0.75	113	90.4	9.6
6	8.27	22.7	1	117	93.6	6.4
7	8.26	22.8	2	119	95.2	4.8
8	8.24	22.9	3	121	96.8	3.2
9	8.2	23	4	123	98.4	1.6
10	8.15	23.5	5	124	99.2	0.8
Average	8.31	22.86				

Table 4: Calculation of Saturation Index of 100 mg/L Ca^{2+} Test for 30 minutes mixing time with PO_4^{3-} inhibitor

Avg. pH	**Temp. (°C)**	**Initial Ca^{2+} (M)**	**kw**	**kA_2**	**CO_3^{2-} as $CaCO_3$**	**CO_3^{2-} as mg/L as CO_3^{2-}**	**CO_3^{2-} (M)**	**Q**	**$\log(K_{sp})$**	**Saturation Index**
8.31	22.86	0.0025	8.58077 E-15	4.47591 E-11	3.612689059	2.167613435	3.61269 E-05	9.03172 E-08	-8.467255741	26.49

Table 5: Findings of experiment with 150 mg/L Ca^{2+} Test for 30 minutes mixing time with PO_4^{3-} inhibitor

Ca^{2+} Test (150 mg/L)						
Mixing Time 30 minutes (Alkalinity = 200, Target Ω = 22.5)						
Sample No.	pH	Temperature (°celsius)	PO_4^{3-} Conc. (mg/L)	$CaCO_3$ 1/2 Hardness (mg/L)	Final Dissolved Ca^{2+} (mg/L)	Final Precipitation (mg/L)
1	7.99	24.9	0	79	126.4	23.6
2	8.02	24.9	0.1	81	129.6	20.4
3	8.07	24.2	0.25	82	131.2	18.8
4	8.09	24.6	0.5	83	132.8	17.2
5	8.03	25.5	0.75	84	134.4	15.6
6	8.03	25.5	1	85	136	14
7	8.39	25.8	2	87	139.2	10.8
8	8.3	25.8	3	88	140.8	9.2
9	8.4	25.9	4	89	142.4	7.6
10	8.27	26	5	93	148.8	1.2
Average	8.16	25.31				

Table 6: Calculation of Saturation Index of 150 mg/L Ca^{2+} Test for 30 minutes mixing time with PO_4^{3-} inhibitor

Avg. pH	**Temp. (°C)**	**Initial Ca^{2+} (M)**	**kw**	**kA_2**	**CO_3^{2-} as $CaCO_3$**	**CO_3^{2-} as mg/L as CO_3^{2-}**	**CO_3^{2-} (M)**	**Q**	**$\log(K_{sp})$**	**Saturation Index**
8.16	25.31	0.00375	1.03664 E-14	4.71068 E-11	2.679917319	1.607950391	2.67992 E-05	1.00497 E-07	-8.480735006	30.40

Table 7: Findings of experiment with 200 mg/L Ca^{2+} Test for 30 minutes mixing time with PO_4^{3-} inhibitor

<table>
<tr><th colspan="7">**Ca^{2+} Test (200 mg/L)**</th></tr>
<tr><th colspan="7">**Mixing Time 30 minutes (Alkalinity = 200, Target Ω =30)**</th></tr>
<tr><th>Sample No.</th><th>pH</th><th>Temperature (°celsius)</th><th>PO_4^{3-} Conc. (mg/L)</th><th>$CaCO_3$ 1/2 Hardness</th><th>Final Dissolved Ca^{2+} (mg/L)</th><th>Final Precipitation (mg/L)</th></tr>
<tr><td>1</td><td>8.8</td><td>25.6</td><td>0</td><td>105</td><td>168</td><td>32</td></tr>
<tr><td>2</td><td>8.8</td><td>25.6</td><td>0.1</td><td>107</td><td>171.2</td><td>28.8</td></tr>
<tr><td>3</td><td>8.8</td><td>25.6</td><td>0.25</td><td>108</td><td>172.8</td><td>27.2</td></tr>
<tr><td>4</td><td>8.8</td><td>25.7</td><td>0.5</td><td>109</td><td>174.4</td><td>25.6</td></tr>
<tr><td>5</td><td>8.8</td><td>25.7</td><td>0.75</td><td>112</td><td>179.2</td><td>20.8</td></tr>
<tr><td>6</td><td>8.8</td><td>25.7</td><td>1</td><td>112.5</td><td>180</td><td>20</td></tr>
<tr><td>7</td><td>8.8</td><td>25.7</td><td>2</td><td>113</td><td>180.8</td><td>19.2</td></tr>
<tr><td>8</td><td>8.8</td><td>25.7</td><td>3</td><td>115</td><td>184</td><td>16</td></tr>
<tr><td>9</td><td>8.8</td><td>25.7</td><td>4</td><td>115</td><td>184</td><td>16</td></tr>
<tr><td>10</td><td>8.8</td><td>25.7</td><td>5</td><td>116</td><td>185.6</td><td>14.4</td></tr>
<tr><td>Average</td><td>8.8</td><td>25.67</td><td></td><td></td><td></td><td></td></tr>
</table>

Table 8: Calculation of Saturation Index of 200 mg/L Ca^{2+} Test for 30 minutes mixing time with PO_4^{3-} inhibitor

Avg. pH	**Temp. (°C)**	**Initial Ca^{2+} (M)**	**kw**	**kA_2**	**CO_3^{2-} as $CaCO_3$**	**CO_3^{2-} as mg/L as CO_3^{2-}**	**CO_3^{2-} (M)**	**Q**	**$\log(K_{sp})$**	**Saturation Index**
8.8	25.67	0.005	1.06542 E-14	4.74499 E-11	11.27999663	6.767997979	0.0001128	5.64 E-07	-8.482784231	171.42

Table 9: Findings of experiment with 75 mg/L Ca^{2+} Test for 30 minutes mixing time with Zn inhibitor

Ca^{2+} Test (75 mg/L)						
Mixing Time 30 minutes (Alkalinity = 200, Target Ω = 11)						
Sample No.	pH	Temperature (°celsius)	Zn^{2+} Conc. (mg/L)	$CaCO_3$ 1/2 Hardness (/L)	Final Dissolved Ca^{2+} (mg/L)	Final Precipitation (mg/L)
1	7.76	21	0	76	60.8	14.2
2	7.65	21	0.1	79	63.2	11.8
3	7.71	20.8	0.25	79	63.2	11.8
4	7.57	21.1	0.5	80	64	11
5	7.67	20.8	0.75	80	64	11
6	7.6	20.7	1	81	64.8	10.2
7	7.49	20.8	2	83	66.4	8.6
8	7.18	20.7	3	84	67.2	7.8
9	7.32	20.8	4	85	68	7
10	7.34	21	5	94	75	0
Average	7.53	20.87				

Table 10: Calculation of Saturation Index of 75 mg/L Ca^{2+} Test for 30 minutes mixing time with Zn inhibitor

Avg. pH	**Temp. (°C)**	**Initial Ca^{2+} (M)**	**kw**	**kA_2**	**CO_3^{2-} as $CaCO_3$**	**CO_3^{2-} as mg/L as CO_3^{2-}**	**CO_3^{2-} (M)**	**Q**	**$\log(K_{sp})$**	**Saturation Index**
7.53	20.87	0.001875	7.33348 E-15	4.28411 E-11	0.577618392	0.346571035	5.77618 E-06	1.08303 E-08	-8.456907721	3.10

Table 11: Findings of experiment with 100 mg/L Ca^{2+} Test for 30 minutes mixing time with Zn inhibitor

Ca^{2+} Test (100 mg/L)						
Mixing Time 30 minutes (Alkalinity = 200, Target Ω = 15)						
Sample No.	pH	Temperature (°celsius)	Zn^{2+} Conc. (mg/L)	$CaCO_3$ 1/2 Hardness	Final Dissolved Ca^{2+} (mg/L)	Final Precipitation (mg/L)
1	7.55	21.8	0	106	84.8	15.2
2	7.71	21.9	0.1	108	86.4	13.6
3	7.71	21.6	0.25	110	88	12
4	7.75	21.8	0.5	110	88	12
5	7.68	22	0.75	110	88	12
6	7.64	22.3	1	112	89.6	10.4
7	7.58	22.1	2	112	89.6	10.4
8	7.47	22.1	3	114	91.2	8.8
9	7.44	22.1	4	117	93.6	6.4
10	7.35	22.9	5	118	94.4	5.6
Average	7.59	22.06				

Table 12: Calculation of Saturation Index of 100 mg/L Ca^{2+} Test for 30 minutes mixing time with Zn inhibitor

Avg. pH	**Temp. (°C)**	**Initial Ca^{2+} (M)**	**kw**	**kA_2**	**CO_3^{2-} as $CaCO_3$**	**CO_3^{2-} as mg/L as CO_3^{2-}**	**CO_3^{2-} (M)**	**Q**	**log(K_{sp})**	**Saturation Index**
7.59	22.06	0.0025	8.05878 E-15	4.39889 E-11	0.679038637	0.407423182	6.79039 E-06	1.6976 E-08	-8.463030946	4.93

Table 13: Findings of experiment with 150 mg/L Ca^{2+} Test for 30 minutes mixing time with Zn inhibitor

Ca^{2+} Test (150 mg/L)						
Mixing Time 30 minutes (Alkalinity = 200, Target Ω = 22.5)						
Sample No.	pH	Temperature (°celsius)	Zn^{2+} Conc. (mg/L)	$CaCO_3$ 1/2 Hardness	Final Dissolved Ca^{2+} (mg/L)	Final Precipitation (mg/L)
1	7.72	21	0	160	128	22
2	7.76	21.7	0.1	161	128.8	21.2
3	7.65	21.7	0.25	162	129.6	20.4
4	7.63	21.9	0.5	163	130.4	19.6
5	7.53	21.8	0.75	163	130.4	19.6
6	7.52	21.8	1	163	130.4	19.6
7	7.6	21.8	2	163	130.4	19.6
8	7.52	21.8	3	164	131.2	18.8
9	7	21.3	4	165	132	18
10	7.16	21.4	5	166	132.8	17.2
Average	7.51	21.62				

Table 14: Calculation of Saturation Index of 150 mg/L Ca^{2+} Test for 30 minutes mixing time with Zn inhibitor

Avg. pH	**Temp. (°C)**	**Initial Ca^{2+} (M)**	**kw**	**kA_2**	**CO_3^{2-} as $CaCO_3$**	**CO_3^{2-} as mg/L as CO_3^{2-}**	**CO_3^{2-} (M)**	**Q**	**$\log(K_{sp})$**	**Saturation Index**
7.51	21.62	0.00375	7.78364 E-15	4.3564 7E-11	0.56098454	0.336590724	5.60985 E-06	2.10369 E-08	-8.460744427	6.08

Table 15: Findings of experiment with 200 mg/L Ca^{2+} Test for 30 minutes mixing time with Zn inhibitor

Ca^{2+} Test (200 mg/L)						
Mixing Time 30 minutes (Alkalinity = 200, Target Ω = 30)						
Sample No.	pH	Temperature (°celsius)	Zn^{2+} Conc. (mg/L)	$CaCO_3$ 1/2 Hardness	Final Dissolved Ca^{2+} (mg/L)	Final Precipitation (mg/L)
1	7.4	24.4	0	110	176	24
2	7.56	24.1	0.1	111	177.6	22.4
3	7.6	24.1	0.25	112	179.2	20.8
4	7.65	24.3	0.5	113	180.8	19.2
5	7.65	24.3	0.75	114	182.4	17.6
6	7.67	24.3	1	114	182.4	17.6
7	7.65	24.4	2	115	184	16
8	7.65	24.5	3	116	185.6	14.4
9	7.45	24.5	4	117	187.2	12.8
10	7.35	24.6	5	118	188.8	11.2
Average	7.56	24.35				

Table 16: Calculation of Saturation Index of 200 mg/L Ca^{2+} Test for 30 minutes mixing time with Zn inhibitor

Avg. pH	**Temp. (°C)**	**Initial Ca^{2+} (M)**	**k_w**	**kA_2**	**CO_3^{2-} as $CaCO_3$**	**CO_3^{2-} as mg/L as CO_3^{2-}**	**CO_3^{2-} (M)**	**Q**	**log(K_{sp})**	**Saturation Index**
7.56	24.35	0.005	9.63168 E-15	4.61894 E-11	0.673135778	0.403881467	6.73136 E-06	3.36568 E-08	-8.475356278	10.06