

CALCIUM CARBONATE SCALING IN PIPES: ANALYTICAL AND EXPERIMENTAL SETTING

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To my Mothers...

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INCRUSTAÇÕES DE CARBONATO DE CÁLCIO EM TUBULAÇÕES: ESTUDO ANALITICO E MONTAGEM EXPERIMENTAL

Paulo Andrés Paz Ordóñez

Dezembro/2015

Orientadores: Theodoro Antoun Netto João Francisco Cajaiba Da Silva

Programa: Engenharia Oceânica

Problemas com acúmulos de minerais oriundos da produção comumente denominados incrustação acontecem frequentemente na indústria do petróleo. Tratamentos químicos, ou intervenções mecânicas são usualmente adotados para combater este problema. Nessa dissertação são estudadas as características mais importantes que potencializam o fenômeno de acumulo de incrustações de carbonato de cálcio em tubulações.

Para explicar a formação de incrustações, foram usadas a cinética da reação química e propriedades termodinâmicas. Foram utilizados testes experimentais em um reator em batelada para estudar a influência que a temperatura e concentração inicial de íons tem sobre o pH da solução do sistema de incrustação. Para monitorar o processo de incrustação alguns métodos baseados no Índice de Saturação das soluções de incrustação alem de um método de análise de imagem foram aplicados.

Além do estudo da reação química, testes dinâmicos foram utilizados para analisar a influência da geometria e taxa de fluxo durante o processo de incrustação. Resultados de testes experimentais de ganho de massa de carbonato de cálcio foram analisados e comparados com os obtidos a partir de métodos analíticos propostos na literatura. Abstract of Dissertation presented to COPPE/UFRJ as a partial fulfillment of the requirements for the degree of Master of Science (M.Sc.)

CALCIUM CARBONATE SCALING IN PIPES: ANALYTICAL AND EXPERIMENTAL SETTING

Paulo Andrés Paz Ordóñez

December/2015

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Problems with accumulation of minerals linked to oil production usually called scales happen frequently in the petroleum industry. Chemical or mechanical treatments are usual to fight this problems. In this dissertation are studied the most important characteristics that improve the calcium carbonate scaling accumulation in pipelines.

To explain the scale formation, the chemical reaction kinetics and thermodynamic properties were used. Experimental test in a batch reactor to study the influence that temperature and initial ion concentration have over the solution pH of the scaling system were run. To monitor the scaling process some methods based on the Saturation Index for scaling solutions and an image analysis method were applied.

Besides the chemical reaction study, dynamic tests were also used in order to analyze the influence of the geometry and flow rate over the scaling process. Results of calcium carbonate mass gain experimental tests and the ones obtained using analytical methods proposed in literature were analyzed and compared.

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Nomenclature

 ρ CaCO3 density, see equation (4.29), page 44

MeOH Methanol, see equation (2.0), page 11

NaCl Sodium Chloride, see equation (2.0), page 11

 k_D Mass transfer coefficient, see equation (4.33), page 44

 $k_{\rm R}$ Crystallization rate, see equation (4.33), page 44

 T_i Scale superficial temperature, see equation (4.33), page 44

DTPMP Diethylenetriamine Penta, see equation (2.0), page 13

HCL Hydrochloric Acid, see equation (2.0), page 12

HP/HT High Pressure/ High Temperature, see equation (2.0), page 9

Ksp Solubility Product Constant, see equation (2.0), page 10

K Equilibrium Constant, see equation (2.0), page 8

LSI Langelier Saturation Index, see equation (2.0), page 10

pHs Saturation pH, see equation (2.0), page 8

PMA Phorbol 12-myristate 13-acetate, see equation (3.0), page 21

PSI Puckorius Scaling Index, see equation (2.0), page 11

QMB Quartz MicroBalance, see equation (2.0), page 14

Re Reynolds Number, see equation (2.0), page 9

Re Reynolds Number, see equation (4.33), page 44

RSI Ryznar Stability Index, see equation (2.0), page 11

Sc Schmidt Number, see equation (4.33), page 44

SDFU Single Stage Flash Distillation Unit, see equation (2.0), page 10

SI Saturation Index, see equation (2.0), page 9

SSMA Sulfonated Styrene-Maleic Anhydride, see equation (3.0), page 21

TEG Triethylene Glycol, see equation (3.0), page 21

Alk Alkalinity, see equation (4.26), page 39

Ca Calcium Ions, see equation (4.26), page 39

EDTA Ethylenediaminetetraacetic Acid, see equation (2.0), page 12

FBRM Focused Beam Reflectance Measurement, see equation (2.0), page 12

I Ionic Force, see equation (4.13), page 34

kf CaCO3 thermal conductivity, see equation (4.29), page 44

n Mass deposition rate, see equation (4.29), page 44

pAlk $-\log([[HCO_3^{-}]/[CO_3^{2^{-}}]])$, see equation (4.26), page 39

pCa $-\log([Ca^{2+}])$, see equation (4.26), page 39

Rf Fouling Resistance, see equation (4.29), page 44

Chapter 1

Introduction

1.1 General

Petroleum industry is one of the biggest and the most important in the world. It's versatility to be used as raw material to feed other industries and as a main energetic source are be the reason. Some products such as fuel, resins, plastics among others are made from the petroleum. It is spread all over the world, although not with equity, and it depends of every individual country, the methods, how it is extracted an so on it's benefits.

Petroleum has had great importance since its discovery in the middle of XIX century. The way how petroleum is extracted has had advances to improve the efficiency. Reservoirs formerly were found into no deep ground and the extraction methods use superficial drilling from where petroleum were obtained without the need for reservoir stimulation.

Since the beginning, having petroleum is a synonym of financial and political stability. It makes that countries invest in knowledge and technology development to keep on top of competitors. With the advance as a premise it was decided that onshore reservoir was not enough and the way to the sea was prospected. It was not a bad idea and soon some of the biggest reservoirs were found off shore in the North Sea and Gulf of Mexico. This one was a great opportunity to Brazil to finally put himself in the eye as a petroleum producer country with importance such as Middle East, Soviet Union and others.

Brazil had one of his biggest discoveries with the Santos Basin at the end of the last century. From this point with his on shore fields, Brazil began to be considered as an important key in the petroleum industry. His focus goes to the sea and it makes to consider the research and tech development importance to keep on going regardless the lack of information about off shore production.

In 2014 the biggest offshore fields in Brazil were the Roncador, Lula and Marlin Sul fields. Just between them reach the amount of 900 Mboe/d [9], as official report this value tops the 90 percent of Brazil's's total production. The Santos Basin, a pre-salt field with high content of carbonates, means one of the most important discoveries. Tupi itself has a recoverable volume of 5 to 8 Bboe, this is just one of many [10].

After Santos Basin, Brazil is looking for petroleum autonomy so starting the XXI century the Pre-salt was discovered. With these discoveries there are a lot of new holes and challenges which has to be fulfilled, new technology has to be developed and the door to a scientific enhancement and research in of shore operations was opened for Brazil.

Some of these challenges refers to the ultra deep water operations, with water barriers up to 2000 m deep, reservoir over 5000 m deep and spread over great areas, even more than 300 km far from shore.

Nowadays the pre-salt production is about 816 MBoe/d and post-salt about to 2280 MBoe/d. The world petroleum production was bigger than 93 MMBdp in 2014 according to U.S. Energy Information Administration.

According to the National Agency of Petroleum, ANP, the oil and gas production in 2014 for Brasil was close to 2497 Mbbl/d and 95,1 MMm3/d respectively, they make a production close to 3096 Mboe/d.

For a variety of economic, environmental and social conditions, there are new challenges to overcome every day. This ought to work always with cutting edge technology in production and exploration processes, even for development of new ones to achieve the goals. In this way, when a process is improved or optimized, it allows in a better way to take advantages and to have better results in production and exploration on a particular field.

Nevertheless, the technological developments still can not solve one of the oldest troubles in production and exploration of petroleum operations, the formation of scales in upstream systems. Scaling is an important issue in the petroleum industry. The mixture of production water and formation or connate water in the fields is inevitable due to of the regular use of production water in production enhancement processes such as water injection. The formation of scales can cause flux assurance problems, emergency blockages and over costs in production and work over, and the most important a fall out of production, for example, British Petroleum lost about 4 Mbbls per year in the North Sea [11].

Water injection process in wells is carried to maintain the inner pressure over the bubble point and also to drive the petroleum to producers wells, in this way having a better petroleum recovery ratio [12]. Some studies have proved that changes in properties such as temperatures, pressure, pH, dissolved gas, usually CO_2 and incompatible water mixture cause to lose chemical and thermodynamic equilibrium in the inner well making that solid particles go bottom and to form scales [13]. Scales grow every day and can cause line blocking. To avoid the blockage of upstream lines there are several methods but unfortunately they are not completely efficients. One of this methods is the usage of chemical inhibitors which delay or stop the scale formation.

There are mechanical methods as well that try to clean the inner wall of the pipes. Currently there are some researches in magnetic and electro magnetic methods which have shown good results fighting scales. When these methods are used, they cause a slower scaling process and a lower quantity of grown crystals. Using procedures like the Tube Blocking Test, is possible to reproduce a scaling process using common ions and to prove the efficiency of inhibitors as chemical treatments to scales.

In order to test some corrective methods to stop the scaling process, a real scale deposition system being created and it is known as LTS Loop. With this Loop to be developed in the Submarine Technology Laboratory it is possible to run experimental tests with similar conditions as int he deep sea. It will also be possible to have temperature variations to provoke, to enhance and more important to control the scaling process.

In addition, as it will be shown in this document, there is the possibility to use analytical methods to identify the possibility of scales on pipe lines happens. Next there are general information about scales:

1.2 Scales Formation

There is plenty of scales types in the petroleum industry. Basic division could be organic and inorganic scales. In the bottom hole and due to of the production of petroleum, the inorganic scales are the most frequently. Those scales are originated by the mixture of incompatible waters, production and formation water, or because of chemical reaction in regard to the ions presented in the fluids and formation itself.



Figure 1.1: Scales in petroleum systems [1].

As you can see in Figure 1.1 there are many kinds of scales, organics and inorganics. Each of one is formed under different conditions, for example: The dissolving CO_2 cause the calcium carbonate scaling, the changes in temperature cause gypsum and barium sulphate scales, changes in the pressure also cause the formation of calcium carbonate and sulphates scales as corrosion is caused by gases too.

The scaling kinetics still is not completely understood. There is a variety of scientific articles that point to eventual accumulation of slayers or even triggered for imperfections in the wall surface of pipes or other equipment. Now it is important to direct the information to calcium carbonate scaling which is the main topic on this project.

1.3 Calcium Carbonate Scales Formation

There are some conditions that trigger the calcium carbonates scaling. The main one is the chemical reaction occurring between the HCO_3^- and Ca^{2+} ions presents in both, formation and production water. It is also formed when there are changes in fluid's temperature and pressure, most accurate the pressure droop dissolves the CO_2 that causes the disequilibrium in the pH of the system and later the nucleation and then the scaling of the calcium carbonate crystals.

To maintain the reservoir pressure close to its natural, water is injected into the reservoir, it could be seawater or fresh water, it depends on the localization of the reservoir. Following this, in offshore operations are injected into the rock which has ions that react and tend to form scales. It is also called connate water, this is because the formation water is part of the reservoir since its beginning. As it is in contact with sediments and barium, strontium, calcium salts. These compounds were located through the time and characterize each reservoir, some of them are more carbonate-ly than others.

In Table 1.1 an example about the composition of sea water and formation water is presented:

Ions	Injection Water Sea water [ppm]	Formation Water [ppm]		
Na^+	10.980	31.275		
\mathbf{K}^+	460	654		
Mg^{2+}	1368	379		
Ba^{2+}	-	269		
Sr^{2+}	-	771		
$\mathrm{SO}_4^{\ 2-}$	2960	-		
Cl^-	19.766	60.412		
Ca^{2+}	428	5038		

Table 1.1: Ions in Sea Water Injection Water - Production Water [8].

The variety of ions presented in the sea water and production water make possible the formation of some other scales besides calcium carbonate.

1.4 Calcium Carbonate Scale Monitoring

Several detection methods for inorganic scales have been tested through scientific investigation. Generally these methods use properties like temperature, solution pH and quantity of dissolved salts or concentration. They are called Saturation Indexes, each one of them shows a qualitative analysis that predict the formation of scales under particular conditions, most of them controlled in experimental setting.

The most common saturation index are the Langelier Saturation Index, LSI, Riznar Stability Index, RSI, and the modifications to the LSI proposed by Stiff&Davies, SI and Oddo&Tomson Index.

These methods take into account the kinetics and the thermodynamic of the chemical reactions involved in the scaling process. This has allowed to develop some analytical models and non commercial software, such as MultiScale, ScaleChem and ScaleSoftPitzer, they are used to study the process. These software show the possibility that scales happens, unfortunately they are not sensible enough to identify the exact place or amount that will affect the upstream systems.

1.5 Objectives

1.5.1 General Objective

To study some analytical models for prevention of scaling phenomena and to correlate with experimental tests. A variety os scenarios of temperature, flux and fluid will be tested with the objective of having experimental database to contest and calibrate the analytical models.

1.5.2 Specific Objectives

- To use analytical and theoretical models to describe the scaling process and to establish the most important parameters to use them correctly.
- To compare the applicability of the models in the oil and gas industry.
- To compare the theoretical and experimental results run in the NQTR Laboratory.

• To design the LTS Loop based on the theoretical models and the experimental tests results obtained.

1.6 Structure of the Study

This study is divided in ten chapters, which are organized in the following way:

Chapter 2 is a theoretical survey containing the analytical and experimental background for the study. It is organized chronologically and scopes the general information about calcium carbonate scaling, Saturation Index, deposition rate and also the theoretical and experimental procedures developed by other authors, information and used methods to monitor the scaling process in real time.

Chapter 3 presents an extended information about the petroleum industry and scaling processes in general, how they are formed and how they are fought nowadays.

Chapter 4 is dedicated to the calcium carbonate chemistry, starting with the way it is formed via chemical reaction, going through the methods to analyze the scales formation and finally the principal experimental ways to monitor the process in real time.

Chapter 5 shows the description of scaling experimental tests that allows applying the analytical methods. The main topic in this chapter is the experimental setting to get sufficient information regard to calcium carbonate scaling. Experimental procedure for qualitative and quantitative empirical methods are described as well.

Chapter 6 shows the results obtained from the scaling tests described in Chapter 5. Results are divided in quantitative and qualitative methods. The influence that system properties as flow rate, pipe diameter, solution concentration have on the chemical process are shown.

Chapter 7 presents a analytical and experimental setting for the LTS Loop. The theories that could be applied to describe its working and the best options to run the experimental scaling tests are presented. Chapter 8 presents Conclusions and recommendations for future researches.

Finally, the Bibliography used in this dissertation is shown along with the Appendices where the experimental and analytical results and Tables that describes most of the considered systems are listed.

Chapter 2

Literature Review

LARSON AND BUSWELL (1943) [14] used the calcium carbonate scaling reaction kinetics to characterize the solutions. They also were able to define theoretically properties like pH, temperature and pressure system. The method used to calculate the saturation index is similar to Langelier's, giving particular importance to the ionic force, alkalinity and pH_s .

HASSON *et al.* (1968) [15] considered the calcium carbonate scaling chemical reaction as a diffusion controlled phenomena. They developed a deposition equation for growth rate based on the first and second dissociation constant of carbonic acid which was correlated with the experimental data showing quite accuracy. Some tests were performed with a heat exchanger, water temperature about 40 °C, calcium chloride and sodium bicarbonate solutions.

NANCOLLAS AND SAWADA (1982) [16] presented a calcium carbonate deposition model based on the chemical reaction equilibrium used to predict the scale growth. They also presented equation for the equilibrium constant K as a function of temperature, between 15 and 45 °C. The possibility of using an inhibitor with phosphate ions resulting in lower scales nucleation were considered.

PRZYBYLINSKI (1987) [17] run experimental tests and he concluded that calcium carbonate deposition rate is controlled by the carbonate ions diffusion. Deposition rate is proportional to saturation ratio which is related proportionally to the total carbonate ions presented in solutions. He said that the CO_2 dissolution and water injection low the medium pH what increases the calcium carbonate scaling.

ODDO&TOMSON (1991) [18] developed a new model to calculate the saturation index for calcium carbonate in aqueous solution. They considered both

cases, with and without gas phase. Those models were made for pipelines in oil and gas industry. They developed methods for pH and SI were based on the calcium carbonate reaction kinetics, it also take into account factors like CO₂ and H₂S presence and HP/HT conditions.

ODDO&TOMSON (1994) [19] based on the chemical reaction kinetics developed a series of equations to quantify the scaling of calcium carbonates via SI. They proposed methods for CaSO₄, SrSO₄, BaSO₄. They also considered the gas phase into the equations.

SULTAN KHAN *et al.* (1996) [20] used a double-pipe counter-flow heat exchanger to make calcium carbonate chemical scaling inside the inner tube. Fluid is heated externally with water and a Constant-Temperature Water-Circulator Bath (CTWCB). They use several diameters for inner tube and temperature settings. A test run is about 2 hours and a experiments consists of 5 tests setting, then the mass gained was analyzed. Fouling resistance was calculated considering experimental settings, flow parameters and thermal conductivity of calcium carbonate. As a result, temperature has an important role in fouling resistance increasing, the opposite for bigger diameters. The flow parameters, like Re has no relevant influence in fouling resistance. Finally they presented an empirical model to correlate the previous parameters.

ESLINGER *et al.* (1998) [21] introduced the scaling problems in oil and gas production. They shown a series of solutions that use fluids and solid particles to remove the scaling in equipments and wells. They run experimental test considering different fluids and solid mixtures which change its roughness. They also mention that the consequences of mechanical methods can affect the integrity of well-bore and pipe system if it is not well set. They conclude that their method does not cause damage, neither well bore nor pipes.

JASINSKI *et al.* (1998) [22] mentioned some methods to calculate calcium carbonate scaling. They compared models using commercial software PHREEQC and others non commercial including the Oddo&Tomson model. They considered different environmental conditions, from low to moderate and HP/HT for the field analyzed.

BUDAIR *et al.* (1998) [23] presented an experimental setting design to analyze calcium carbonate scaling in 0.5" diameter tubes. They got a correlation between the solution concentration at the beginning, the mass that was deposited and the

experimental time. They used Re number to control the flow set. They also used fouling resistance theory to monitor the scaling process in real time measuring the superficial temperature of the pipes.

PEREZ AND POLIZZOTTI (1999) [24] studied different kind of scales found in Single Stage Flash Distillation Unit (SDFU). It provided a real measure and a treatment program to prevent scale under heat transfer conditions. They used synthetic sea water with ions like calcium, magnesium, strontium, among others. It was run a control test without inhibitor to measure the layer of scales, and then several inhibitors were used and compared to get the most effective one. The best one is a multicomponent treatment consistent of a co-polymer of maleic acid, a phosphonate based compound and a polymaleic anhydride.

ZHANG AND FARQUHAR (2001) [25] set a Tube Blocking Test for calcium carbonate scaling and analyzing the inhibitors performance. They considered the performance of the inhibitor in time, and compare it with control tests without inhibitor. They analyzed the SI of solutions used, and also they compared them with a reservoir data. They even mentioned a developed kinetics model to predict the scaling, it was not shown in the paper.

FERGUSON (2002) [26] proposed to use SI to quantify scaling. His theory was demonstrated with calcite scaling and LSI. He used this index to describe the possibility of oxalate scaling, he also used additional information such as K_{sp} and initial concentration of salts. He was able to correlate the possibility of scaling with the temperature and solution pH.

BEZERRA *et al.* (2002) [27] established a sulfates scaling system based on real information from some wells in Brazil. They analyzed the scaling in risers and reservoirs, using their chemical and thermodynamic conditions. They used commercial software like OkScale and MultiScale to model analytically the scaling tendency. The experimental test were dynamic core flooding test.

MOGHADASI *et al.* (2003) [28] developed a general review of scales presented in oil and gas production operations. They used the reaction kinetics of crystal formation for various carbonates and were able to model a scaling process to analyze some wells.

BOUDREAUX *et al.* (2005) [29] presented a new mechanical method to remove barium sulphate scales in tubes. It was a new development which has shown good results in removal and structural damage.

RAMSTAD *et al.* (2005) [30] presented a temperature, pressure and salt composition analysis for different reservoirs with previous scaling troubles. Those conditions were use to model in MultiScale software to a particular reservoir. They developed a monitoring scaling system. Using te reservoir characteristics they made synthetic water and then run some scaling tests inside a equipment with an in line camera to follow the scaling process. This equipment has pressure and injection fluids controlled.

CHEN *et al.* (2004) [31] designed a calcium carbonate scaling system using a controlled concentration solution and a stainless steel electrode as a body test. They considered different initial concentrations and tests time. They developed a correlation between the electrical properties of the electrode under scaling conditions to monitor the process.

CAVANO (2005) [32] presented a theoretical study using *SI*, *RSI*, *LSI*, *PSI* among others. He also presented the best scaling control methods as chemical inhibitors. He also enumerated the most used chemicals in scaling treatment.

SHIPLEY *et al.* (2006) [33] was aiming to make inhibition with scaling test using several mineral salts like calcite, sulphates, halite. They used prediction models based on the activity coefficients of compounds in chemical reaction as SI varying the concentration of MeOH and NaCl as inhibitors. They used the ScaleSoftPitzer software for analytical modeling.

ALIMI et al. (2007) [34] run experimental tests to analyze the influence of magnetic field over scaling processes. They found that the magnetic field has influence over the solution pH and also over the ratio of precipitation which they calculated using the initial concentration of ions in solutions and the final one after tests. They also consider the effect of water flow and it's incidence in nucleation and precipitation of calcium carbonate.

TAHERI *et al.* (2008) [35] presented experimental test and simulations of damages that occur in presence of mineral scaling. They used information from the Sirri-C offshore oil field in the Persian Gulf. They performed experimental tests using water solutions with similar composition to formation and injection water. The data log included temperature, solution pH. They used the Moghadasi *et al* (2003) [28] study about *SI* to predict the scaling. They used CMG-STARS 2005 Software to model the effects of scaling into reservoirs. Different pressure and temperature scenarios were considered by them, P[2500-4500]psi and T[50-100] °C.

LARSEN *et al.* (2008) [36] used core flooding experiments to reproduce the calcium carbonate scaling problems in reservoirs. They followed the SI at the end of the core and analyzed its change over time. The core were flooded with $CaCl_2$ and $NaHCO_3$ solutions with de-ionized water. They also used porosity models and parameters to analyze the scales formation.

AL NASSER *et al.* (2008) [37] proposed an experimental technique to quantify calcium carbonate scaling. They used a FBRM equipment that uses a laser to measure the crystal ratio and make an statistical analysis of crystals media size distribution. They concluded that his objective it is not to measure the crystal ratio but the scaling depositions process, but also the great influence that the initial salts concentration has over the scaling process even more than temperature has.

QUAN Z. et al. (2008) [6] developed an on-line monitoring system of fouling resistance caused by calcium carbonate scaling in heat exchangers. For each experiment superficial pipe and fluids temperature, electric conductivity and pHwere measured. The calcium and bicarbonate concentration was measured by EDTA titration and HCl respectively. After the scaling test the tube where it happens was removed, dried and weighted to obtain the deposited mass. They used a heat transfer analysis to obtain the fouling resistance. over time.

TOMSON *et al.* (2009) [38] started exploring reservoir problems. They used mass transfer theories along with chemical equilibrium equations to propose a SIdependent of pressure and temperature. They considered the calcium carbonate scaling as a mass diffusion problem. They also presented simulations and analytical calculations using the ScaleSoftPitzer software for a core.

SENTHILMURUGAN AND GHOSH (2009) [39] used a co-polymer as inhibitor for calcium carbonate scaling which efficiency was validated and qualified as high.

LIMA (2010) [12] presented a Master Thesis whose objective was to identify what kind of scales a tube has. He used a spectrophotometric technique with C-Ray Fluorescence that identifies the scaling morphology and quantifies crystalline phases using statistical patterns. The Rietveld method was used to analyze and quantify the proportion of scales. The experimental tests were made with grounded scales obtained from scaled tubes. GUAN (2010) [40] used the MultiScale package to show the importance of studying scaling process designing nine real case scenarios. He recalled the use of trustful data to have good results. They also shown that the pH has big deal with the scaling prediction. Reservoir, down-hole, wellhead ant other points properties were used to run the software.

LU et al.(2010) [41] run experimental tests to prove the efficiency of chemical inhibitors. They used reaction kinetics and SI theory to make the numerical analysis for the considered processes.

BAHADORI (2011) [42] made a MatLab language based program to calculate the SI using seawater and production water mixtures properties. An example with dissolved CO₂ influence, which increase properties as pH and helps the calcium carbonate scaling happens was presented. The theory presented by Chilingar *et al.* (1968) [5] for K dependent of ionic force and temperature, also the models presented by Langelier (1936) [43] and improved by Stiff&Davies (1952) [44] were used. They finally presented a MatLab interface which is feed with information like temperature, pressure, ions concentration to solve and present the SI.

ESEOSA *et al.* (2011) [11] explained the effects that properties like pH, temperature, ionic force and pressure have over the calcium carbonate scaling. They used the *SI* proposed by Langelier and Stiff&Davis. They used the properties from an unspecified well in the Scale-Check Software to monitor the scaling process. They used temperature and pressure between [150-250] °F and [355-500] psia.

ZHANG *et al.* (2012) [45] proposed a dynamic model to monitor the calcium carbonate scale process theoretically, this model takes into account initial, in the equilibrium and final concentrations. They established the scaling as a diffusion controlled mass transport phenomena. They performed experimental tests using carbon steel tubes with test time from 4 to 14 hours. They calculated the mass transfer coefficient considering flow parameters and the Sieder and Tate correlation. They also tested some inhibitors as DTPMP.

LIU et al. (2012) [46] designed an hypothetical production water and sea water mixtures that can cause scaling, in this case calcium sulphate and barium sulphate. The analysis were made using Scale Prediction Results software and results for SRand mass deposition were obtained. The experimental tests were run in a loop for tube blocking test setting. The increasing pressure to the top limit of the device was monitored. The efficiency for some inhibitors in time was evaluated. The SI from the software was compared with the experimental SI having good correspondence.

JING G. AND LI XIAOXIAO (2013) [47] developed an experimental method to study the electromagnetic and magnetic field effects acting as an anti-scaling process for calcium carbonate. They also used a pair of commercial inhibitors to test their efficiency. Calcium concentration was measured with EDTA titration used to find the formation rate of calcium carbonate. They concluded that the calcium carbonate concentration decays slower with the electromagnetic treatment.

MAVREDAKI (2014) [48] used a quarts micro-balance to monitor the calcium carbonate scaling. He created calcium and bicarbonate brines and based on the SR analyze the possibility to produce scales, they also analyzed the induction time of each case. With the QMB to know the quantity of calcium carbonate scale mass on time was possible.

PÄÄKKÖNEN *et al.* (2014) [49] run experimental tests for calcium carbonate scaling in heat exchangers and they also measured the fouling resistance to monitor the process. Their objective was to follow the scaling process under different flow and temperature conditions and also the uncertain with the use of experimental data base with mathematical models proposed. Several models to compute the mass deposition rate and the fouling rate based on flow condition were used, solution properties and superficial temperatures along the tubes where the brines are conducted were measured.

Chapter 3

Scales

3.1 General Information

Tupi Well, in Santos Basin area, is one of the biggest discoveries in the pre-salt era, about 5200 m deep with a distribution as follow: A 2126 m water barrier, a 1000 m post-salt barrier and a 2000 salt barrier. At this point was possible to find a field with great potential for exploration and production operations.

With conditions like these, problems as casings collapse, tube blocking and some other completion issues are frequent. Among with those, there are some production troubles. The systems used for pre-salt and post-salt operations are production lines, this lines are tubes usually made of steel; they could be rigid or flexible depend on their objectives.

Pipelines are used to transport petroleum fluids as formation water, production water, oil, completion fluids, among others. Due to their chemical characteristics and ions presence some chemical reactions happen inside the lines producing scales in the tube walls. Over the time those scaling begin blocking the tubes and causing flow assurance troubles.

It has to be considered that the environment this pipelines are working on is hard. The deep sea and the long distances make difficult work over and maintenance operations, due to this conditions is necessary to design methods to control or to avoid any problems, particularly scaling.

Theoretical information regard to scaling is presented in this Chapter. The purpose is to show methods that are currently used to identify or monitor scaling process. From this point on there is some important properties that determine the possibility of the scale formation like pressure, temperature and solutions concentration control.

Figure 3.1 shows a pipe with calcium carbonate scaling.



Figure 3.1: Pipe with calcium carbonate scaling [2]

3.1.1 Economy of Scaling

Economic costs around scaling are related to treatments in order to control or to solve scaling issues, also include loses caused when systems no treated on time, ending in production inconveniences. For example, in the North Sea, in the Miller field, production went from 30 MBo/d to zero in approximately a day because scaling problems. In this way is possible to calculate the economic loses due to of production delays [50]. According to data, costs for clean a production system and starts to work normally again is comparable with chemically treating the entire field.

All mitigation, correction or avoiding processes have costs, the difference resides if they are treated on time, there is the possibility to avoid the loses for production delays, this makes the prevention processes being cheaper than correction processes.

3.2 Organic and Innorganic Scaling

Considering all the fluids petroleum industry work with, it is difficult to completely avoid the scaling problems, said that, there is research surrounding the delay of this scales in transport fluids processes or even try to mechanically eliminate them when the blocking process is still beginning.

To delay the scaling processes has been used chemical treatments with inhibitors. There is also research projects using pigs to crack the scales in order to clean the tubes and new treatments using magnetic and electromagnetic devices which creates a magnetic field that acts over the solid particles and does not allow them to stick hardly and make easier to clean them up even just with the flow itself without the opportunity to start scaling and possible blocking.

It is important to say that there is several kinds of scaling and they depends on the reservoir nature and environment. In general, the scales have been focus of many studies, starting with the thermodynamic and kinetics, then going to know the approximately amount and morphology of the formed scales.

Some kind of scales are the hydrates, some of them as carbon hydrate are formed with presence of CO_2 within the well. Find barium sulphate and paraffins is easy as well. Any of this substances cause blockages in pipelines for production or exploration processes. Even though, the interest in this project is the calcium carbonate scaling.

Scaling problems are frequently caused by temperature and pressure changes inside the well, the pipelines and reservoirs. Also because of the exchange and dissolving of gas phase containing CO_2 and H_2S which cause a change in the solution pH and produce eventual accumulation of crystals nuclei that come together growing and precipitating later.

To solve some issues like pressure drop inside the reservoir there are processes like water injection, usually production or sea water. This process is also used to improve the recovery factor and to maintain the production level that is affected by pressure drops. It is well known that the pressure within the reservoir gradually decrease, the flow ratio and petroleum recovery as well [51].

Nevertheless the injection water is a production enhancement method for petroleum industry, it causes scaling in wells, pipes and reservoir. There are ions of barium, strontium, calcium and magnesium in the rock pores that can cause a super saturated system which cause the precipitation and calcium carbonate, barium sulphate, strontium sulphate and magnesium carbonate scaling inside the pipelines. These compound precipitates when there is ideal thermodynamic conditions in presence of formation or production water injection [52]. The precipitation of those salts is a consequence of low solubility and super saturation of each of them in water [53].

Table 3.1: Most common scales in oilfields			
Scale	Chemical Formula	Conditions	
Calcium Carbonate Calcite	$CaCO_3$	CO_2 parcial pressure, temperature, TDS, pH	
Calcium Sulphate Dihydrate Hemihydrate Gypsum	$\begin{array}{c} \mathrm{CaSO}_3 \cdot 2\mathrm{H_2O} \\ \mathrm{CaSO}_4 \cdot 0.5\mathrm{H_2O} \\ \mathrm{CaSO}_4 \end{array}$	Temperature, TDS, pressure	
Barium Sulphate Strontium Sulphate	$\begin{array}{c} \operatorname{BaSO}_4\\ \operatorname{SrSO}_4\\ \end{array}$	Temperature, pressure TDS	
Iron compounds Ferrous Carbonate Ferrous Sulfide Ferrous Hydroxide Ferric Hydroxide	$\begin{array}{c} \mathrm{FeCO}_{3} \\ \mathrm{FeS} \\ \mathrm{Fe(OH)}_{2} \\ \mathrm{Fe(OH)}_{3} \end{array}$	Corrosion, dissolved gas, pH	

Table 3.1 shows a variety of scales and the medium, thermodynamic and chemical conditions they are formed in:

In this dissertation only the calcium carbonate scaling was considered taking into account that its chemistry allows to remove them in an easier way than other scales as barium sulphate which particularly could block permanently the pipes used in experimental tests.

3.3 Equipments Damages

As a flow assurance problem, the calcium carbonate scales are commonly present in equipments that conduce fluids. Chemical characteristics of the fluids, changes in pressure and temperature, as said before, helps the scaling, up next are shown some problems frequently presented in equipments:

3.3.1 Heat Exchangers

In heat exchange systems, water is normally used as a cooling fluid going inside the tubes. High temperature conditions makes the water evaporates over time and mineral concentrations increase, when it arrives to the solubility limits there is salt precipitation and scaling in the tubes walls. In this way is formed a slay of mineral scaling, commonly calcium carbonate.

A drop in the heat transfer efficiency and a variation in the out temperature of fluids over time are typical characteristics on heat exchangers with scaling problems. Besides, the energetic loses are significant. There is information that electric consumption grows for about 30% every millimeter of scaling thickness and also an increasing in the thermal resistance, that is how the concept of Fouling Resistance for heat exchangers was created.

3.3.2 Risers - Pipelines

The pipelines dedicated to production and exploration are usually blocked by scaling as they work permanently with fluids, this cause huge economical loses.

An industry where about 30% of the operational costs are related to the pipelines use, the problems with calcium carbonate scaling is one of the main no be controlled or corrected.

3.4 Scaling Correction

Unfortunately the scaling problem has no a permanent solution yet. Even though it does not mean that can not be used preventive or corrective treatment to reduce the damages caused by those crystals.

This so called solutions have to act quickly and cause no harm to the well, reservoir or to the pipeline system. Every problem has to be analyzed taking into account the characteristics and environmental conditions where the solution will be applied.

Some known treatments which are commonly used nowadays to correct the scaling problems are listed next:

3.4.1 Physical Methods

Mechanical or physical methods are the most commonly used for scaling removal, they can be by perforation, milling or jetting. Using impact methods as milling is
common when there are thicker scales. Those are methods used inside the wells and pipeline systems when possible [1].

When the pipelines systems conditions or configurations do not allow the use of milling, it could be used jetting as scale removal.

3.4.2 Jetting Cleaning

Abrasive methods are actioned at the same time as exploration or completion tools. These have good performance over porous and brittle scales. They present a body with a rotary head with velocity control. The newest have weigh charges to improve performance. Something interest is that the body only can keep going inside the pipe when cleaned and scaling free.

It is possible to use chemical cleaners to improve their efficiency. In jetting systems also can be used fluids with grave or sand as abrasive mixtures. Generally the fluid is mixed with particles that for mechanical action remove the scales and clean up the affected systems but can end up in structural damage inside the tubes because of the excessive abrasiveness and roughness of some particles as sand or grave [21]. A common problem is that solid particles can affect directly the tubes causing damages like erosion in the wall pipes. To avoid this additional problem new materials for solid particles are being researched as silver particles which are efficient with cleaning and do not affect the tubes in similar way that sand.

Figure 3.2 shows a jetting system.

3.4.3 Chemical Methods

Chemical methods are used to solve scaling problems in wells when the mechanicals are no convenient, also these chemical methods are cheaper than the formers.

A positive characteristic about calcium carbonate scaling is its solubility, that is why the chemical treatment usually selected is the dissolving of calcium carbonate scaling with HCl, even is not the better, as it can affect the integrity of pipelines and equipments because of its reactiveness.



Figure 3.2: High Impact Rotary Jetting Tool

3.4.4 Inhibitors Treatment

Usually scaling inhibitors are chemical agents that act reducing the size of the particles or crystals and stopping or delaying the nuclei or suns formation that cause the scaling.

The use of inhibitors for calcium carbonate formation in pipelines has to be studied and has to be done carefully, it is necessary to choose the right inhibitor in order to do not cause more damages. The most used inhibitors are organic compounds like methanol, ethanol, ethylene glycol and TEG. This are used to avoid the gas hydrates in oil and gas operations, unfortunately the cause the precipitation of others like carbonates or sulphates.

Another inhibitor used to correct the scaling in pipelines are phosphonate compounds, polyphosphate, amino phosphate, ester phosphates among others.

One of the hypothesis is that the inhibitor modify the nucleation and grow rate of scales, in that way the particles that form the suns do not adhere to the pipeline walls [54].

There is a group of inhibitors called Crystal Modifiers which avoid the scaling and cause the crystals to form a moody or minor crystals. Inside this group there are the *PMA* and the *SSMA*. The chemical inhibitors used have tow steps. After to implement a scaling elimination process as treatment to not allow them to come back and as a treatment to avoid this problem does not occur. The inhibitor effectiveness is related with the saturation ratio of the system of interest.

There is two ways the inhibitors can act. First consist in the reaction between the cation, in this case the calcium ion, and its concentration decreases and stop the calcium carbonate formation. The other way is to affect directly the crystals growing. The first is more expensive, it has to be stoichiometric and the quantity of ions inside a reservoir is huge.

The most common methods to administrate the chemical inhibitors are directly inside the well, injection with gas lifting treatment and some others.

It happens that the solution containing the inhibitor is injected into the reservoir and eventually goes to the production water, pipelines and well. It is expected that the inhibitor acts gradually and in long term. It is necessary that the inhibitor does not affect the production and resist the operation conditions.

3.4.5 Magnetic and Electromagnetic

They represent new methods with great possibilities offering a better scaling control. The main idea is to modify the scaling kinetics avoiding the accumulation and formation of the crystalline layer.

These methods has been studied as a replacement for chemical treatments. Besides, some devices that emit magnetic and electromagnetic fields has been used, the inconvenient for this is the need of electrical feeding, cooling and work over in ultra deep water conditions.

Chapter 4

Calcium Carbonate Scaling

In this chapter was made an introduction to the calcium carbonate scaling problem located in oil and gas production systems. Therefore, this chapter is dedicated to the chemical information regard to the calcium carbonate scaling process, including formation, detection.

There will be given some characteristics to understand the scaling chemistry and some methods to evaluate, using the well conditions, the possibility to scales occurrence. It also will be given more deep information about the chemical process and practical methods to detect and control the scaling problems on time.

Calcium carbonate scales were produced by chemical reaction between the calcium chloride and sodium bicarbonate. Is one of the most common scales found in oil and gas pipelines worldwide, especially in Brazil where his field has carbonate characteristics.

To understand the scaling occurrence are proposed some methods like Langelier [43] who proposed the LSI. As the scaling process is complex, the LSI is used to determine the possibility of occurring the calcium carbonate precipitation in water. LSI is used to describe the aqueous phase saturation state against the dissolved solids.

There are some analytical methods that measures the possibility of scaling based on the chemical conditions, temperature, pressure and salt concentration. The LSI parameter allows to estimate the precipitation potential to different solids in an balanced aqueous phase. If LSI is negative, the system is not saturated an the precipitation does not occur, if LSI is equal to zero, the system is in equilibrium and if LSI is bigger than zero, the solution is in an over saturated state which drives to calcium carbonate precipitation and possibly a scaling problems [42].

4.1 Calcium Carbonate polymorphisms

Calcium carbonate is a chemically inert mineral with alkaline characteristics. It has several morphologic structures with the same chemical composition but different physical properties. The most stable crystal polymorph is the calcite. This among with vaterite and aragonite are the calcium carbonate polymorphisms.

The developing of each structure is influenced by temperature which affect the number of crystals and its hardness. Now a brief description of calcium carbonate polymorphisms.

4.1.1 Calcite

The calcite crystal structure is trigonal, presents several colors when contaminated with other metals that replaces the calcium ion. Calcite grows slay over slay. It is produced by calcium carbonate precipitation between 15 y 25. It is the less soluble.

4.1.2 Aragonite

This polymorph is the most thermodynamically stable at high pressure condition. The aragonite crystals are harder than calcite's. It is possible to produce aragonite with the precipitate of a calcium carbonate solution with a temperature between [60-90] °C. Its crystalline shape is orthorhombic.

4.1.3 Vaterite

It is the less stable of calcium carbonate polymorphisms. It is possible to obtain with the precipitate of a calcium carbonate solution with a temperature between [25-40] °C.

Table 4.1 enlists a description of all polymorphisms most important properties.

Property	Calcite [55]	Aragonite [56]	Vaterite [57]
Chemical Composition	CaCO ₃	CaCO ₃	CaCO ₃
Stability	Stable	Instable	Instable
Density	2,711	2,947	2,645
Hardness	3	3,5-4	3
Fusion Point [°C]	1339	825	
Crystalline Shape	Trigonal	Orthorhombic	Hexagonal
$Ksp~(25^{\circ}C)$	3,31E-9	4,61E-9	1,22E-8
Solubility [mg/L]	5,76	6,8	11,04
Color	White, gray, yellow, green, transparent	White, red, yellow, orange, green, gray, blue, purple and brown	Transparent
Specific Gravity	2,71	2,91	2,54

 Table 4.1: Calcium Carbonate Polymorphisms Physical Properties

Figure 4.1 shows the quantity of each calcium carbonate polymorphisms as a function of the solution temperature. As seen before in Table 4.1 each of them have particular properties and stabilities that take the $CaCO_3$ into a different state or polymorph.



Figure 4.1: Abundance of crystalline calcium carbonates as a function of temperature [3].

4.2 Calcium Carbonate Scaling Formation

Between al the polymorphisms of calcium carbonate, the calcite is the most common scale type. Usually formed by CO_2 dissolving from water and causing an unbalanced thermodynamical and chemical state that takes to the reaction of bicarbonate and calcium ions precipitating calcium carbonate. The well environment could produce a mixture of polymorphisms.

Several processes drives to the calcite formation, they are describe as follows:

4.2.1 Water Mixtures

The principal water mixture is the union between formation and production water. Reservoir rocks have water trapped inside their pores since the sedimentation process. When production and exploration start, this water transforms into formation water that goes outside the reservoir. When freed, the formation water can react with the rock under temperature and pressure effects, also the chemical composition of the reservoir influences reactions that becomes inconvenient for downstream operations. The chemical properties for the formation water depends of the environment it was developed in. The most common ions presented in formation water are sodium, magnesium, calcium, potassium, strontium, barium, iron, chloride, sulfate, bicarbonate, carbonate, hydroxide, phosphates, some acids and dissolved gases.

In off-shore operations, the sea water is injected to maintain the reservoir pressure to keep on going the petroleum production levels. Sea water is charged with ions chloride, sodium, sulfates, an others, resulting in an unbalanced chemical equilibrium and causing reaction between the ions and driving precipitation of mineral crystals and scaling. It could happens inside the reservoir when water is injected directly in it, this cause troubles that even could lead to close the well for blocking, also the deposition in pipeline systems is possible.

4.2.2 Chemical Process

After a introduction to scaling problems is important to show how the calcium carbonate scales are formed.

A typical reaction for calcium carbonate formation is shown in Equation 4.1.

$$\operatorname{Ca}_{(\mathrm{aq})}^{2+} + 2\operatorname{HCO}_{3}^{-}_{(\mathrm{aq})} \Longrightarrow \operatorname{CaCO}_{3(\mathrm{s})} + \operatorname{H}_{2}\operatorname{O} + \operatorname{CO}_{2(\mathrm{aq})}$$
(4.1)

At first, CO_2 dissolved in water is in equilibrium with CO_2 in gas phase. When the system begin to gain temperature the CO_2 solubility decrease, it is freed from the water and cause the change of the solution pH which makes the calcite solubility to decrease as well and starts precipitation and calcium carbonate scaling. Said in a better way, temperature change cause the reaction equilibrium goes to the right and helps the $CaCO_3$ precipitation.

This can be explained as follows: The reaction shows that the pressure is important to this kind of reactions. With the pressure drop caused by the oil production, the solution stays under effects of a low bubble point pressure which causes the dissolving CO_2 .

The reaction will be influenced to produce more CO_2 , to the right, by the Le Châtelier Principle, whis says that "Any change in status quo prompts an opposing reaction in the responding system", in this way the reaction will redirect to a balanced position, for example the CaCO₃ precipitation under CO_2 in excess.

What first happens is that the calcium carbonate reach over-saturation and starts its deposition, the formation of nuclei and adhesion of each of them to another make them grow and finally there is crystal formation and scaling.

In any scaling process there is a primary and a secondary nucleation. The former happens due to the solution saturation and is when the very first crystals appear. The secondary nucleation is influenced by the presence of crystals already formed which can act as seeds and promote the union and growth of the crystals.

Figure 4.2 shows the process describe lately:



Figure 4.2: Calcium Carbonate Nuclei to Crystals [4]

Resuming, condition as increasing temperature, pressure dropping, CO_2 dissolving and increasing solution pH could cause and eventual $CaCO_3$ precipitation and possible scaling in pipelines and other equipment used in petroleum production operations.

It is important the analysis of the characteristics on most favorable conditions to scaling and the precipitation kinetics which try to determine the deposition rate and the chemical reaction mechanism that makes it happens.

This kind of analysis helps to await the point where is possible to happens the scaling, for example, in the reservoir, in the production columns, in process plant, in process equipments, in pipelines and others.

Some of the principal characteristics to favor the scaling are listed next:

• Compounds concentrations and properties, ions Ca^{2+} , HCO_3^{-} , etc. Salts with

common ion effect with Ca^{2+} reduce the calcite solubility.

- Presence of another species like catalysts, inhibitors, retardants. There is evidence of co-precipitation between calcium carbonate and barium sulfate, besides the retardant action of NaCl when present in high concentration in the solution treated. The presence of NaCl increases the solubility of calcite till a concentration of 120 mg NaCl / 1000 mg H_2O , if it is overcome, the calcite solubility drops.
- Contact ares inside pipelines wall.
- Partial pressure of CO₂
- Flow turbulences cause calcite precipitation

4.3 Chemical Equilibrium

The chemical equilibrium describe the state when the direct reaction rate, to the products, is equal to the inverse reaction rate, to the reagents. It means, in an reaction in chemical equilibrium state there are reagents that react and form products at the same time when the products react inversely and go back to be reagents at the same rate, this is why the composition in equilibrium state remains constant.

Up next it is show how the equilibrium for calcium carbonate formation has been establish, as well as the species that interact as reagents and products.

A simple reaction for calcium carbonate formation is shown in Equation 4.2.

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_{3}^{2-}_{(aq)}$$

$$(4.2)$$

According to Equation 4.2 there has to be taken into account the reaction that describes the calcium carbonate formation mechanism, as follows:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$$
 (4.3)

The CO_2 goes from gas phase to aqueous so is possible for it to react with water, as shown in equation 4.3, to produce the $H_2CO_{3(aq)}$ as shown in Equation 4.4.

$$\mathrm{CO}_{2(\mathrm{aq})}^{+}\mathrm{H}_{2}\mathrm{O} \Longrightarrow \mathrm{H}_{2}\mathrm{CO}_{3(\mathrm{aq})}$$
 (4.4)

The $H_2CO_{3(aq)}$ is formed when having the acidic condition and happens the first proton dissociation. Then the $HCO_3^{-}_{(aq)}$ is formed as shown in Equation 4.5.

$$H_2CO_{3(aq)} \rightleftharpoons H^+(aq) + HCO_{3(aq)}^-$$
 (4.5)

The second proton dissociation forms the $\text{CO}_3^{2-}_{(\text{aq})}$ ion as shown in Equation 4.6.

$$\mathrm{HCO}_{3(\mathrm{aq})} \rightleftharpoons \mathrm{H}^{+}(aq) + \mathrm{CO}_{3(\mathrm{aq})}^{2-}$$
(4.6)

With the $\text{CO}_3^{2-}_{(\text{aq})}$ ion, is possible to react with the $\text{Ca}_{(\text{aq})}^{2+}$ ion and produce the $\text{CaCO}_{3(\text{s})}$ which depending on the solution conditions can precipitate or stay soluble.

The species that intervene in the calcium carbonate formation process are maintained in chemical equilibrium through the process. The quantity of each specie depends of the solution conditions, acidity, alkalinity. A typical equilibrium system for the calcium carbonate is shown in Figure 4.3.



Figure 4.3: Calcium Carbonate Equilibrium Species [?]

Changes in conditions as temperature or pressure affects the formation of one or another component. It is necessary to stand that the equilibrium and the presence of one or more species depends on the solution pH as it can be seen in Figure 4.3.

Temperature and pressure play an important role in the calcium carbonate equilibrium system. When temperature increases, calcium carbonate precipitates and pH decreases, at the same time when pressure drops there is CO_2 dissolving, so it changes the pH, because of that there is a constantly fight between the involving chemical equilibrium reactions.

4.3.1 Equilibrium Constant

Constant equilibrium, denoted as K, shows the relation between reagents and products involved in a chemical reaction when the equilibrium is reached. Depends of temperature and ionic force.

K value can be found using the activity of reagents and products, but can be used concentration and partial pressure as well. Equations that give K for the first and second proton dissociation in calcium carbonate chemical reaction mechanism are shown next:

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \tag{4.7}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^{-}]} \tag{4.8}$$

As seen in Equations 4.7 and 4.8, K can be calculated using concentration species in the equilibrium. These concentrations have to be measured experimentally and having into account the chemical kinetics for each reaction, even though there are some empirical equation that describes the K value efficiently.

$$log K_1 = -356, 3094 - 0,06091964T + \frac{21834,37}{T} + 126,8339log T - \frac{1684915}{T^2}$$
(4.9)

$$log K_2 = -107,8871 - 0,0325849T + \frac{5151,79}{T} + 38,92561log T - \frac{563713,9}{T^2}$$
(4.10)

Equations 4.9 and 4.10 represents empirically the K_1 and K_2 constants respectively. They are dependents of the temperature solution.

4.4 Salts Solubility

The concept of solubility refers to the quantity of salt that stays dissolved in an amount of water under particular temperature and pressure conditions. Those conditions can help to increase or decrease the solubility, it depends on the chemical kinetics of each salt or compound.



Figure 4.4: Salts Solubility vc Temperature

Figure 4.4 shows the effect that temperature has in the solubility of some salts, there is also an example of revers solubility for calcium carbonate in water. The calcium carbonate solubility presents an inverse behavior, meanwhile several salts increase their solubility with temperature, to de calcium carbonate occur the opposite.

4.4.1 Constant Solubility Product

Denoted as K_{sp} , the constant solubility product is an equilibrium constant for a solid substance that can be dissolved in an aqueous solution. It represent the point till the solid can be dissolved under determined conditions of temperature, pressure, solution concentration, among others. The higher the K_{sp} , the more quantity of solid can be dissolved.

The K_{sp} for calcium carbonate may be obtained from Equation 4.2 and is expressed as follows:

$$K_{sp(CaCO_3)} = [Ca^{2+}][CO_3^{2-}]$$
(4.11)

Note that Equation 4.11 depends on the ions concentration involved in the

chemical reaction. If the ions has coefficients, this becomes the concentration exponent in the K_{sp} equation, also the exponent for pure substance, as solid CaCO₃, the exponent is zero and those are not considered in the K_{sp} equation.

The K_{sp} values are constant for a particular system in equilibrium, it means, temperature, pressure, concentration ions conditions will change its value. Up next some behavior examples about it.

Temperature and Pressure Effects

As the temperature has effects over the salt solubility, it also has effects over the K_{sp} . To understand the behavior of the calcium carbonate scaling reaction with temperature is possible to compare the K_{sp} value.

Thaeri *et al.* [35], present experimental results of calcium carbonate scaling with pressure, temperature and ionic force changes, and propose the next empirical equation for K_{sp} .

$$pK_{sp} = 7,82+6,46*10^{-3}T+8,59*10^{-6}T^2-7,00*10^{-5}p-3,21*\sqrt{I}+1,073I \quad (4.12)$$

$$pK_{sp} = -\log K sp \tag{4.13}$$

They were able to identify that calcium carbonate Ksp is inversely proportional to temperature, which means the scaling increase with the temperature. The ionic force is a fluid property and depends on the ions concentrations, its effect is not big enough on time but with changes in initial ion concentration.

I represents the ions concentration in a solution. Influences the solubility and other properties. It is expressed as follows:

$$I = \frac{1}{2} \sum_{i=1}^{n} m_i z_i^2 \tag{4.14}$$

According to Chilingar *et al.* [5], I can also be found multiplying the ion concentration to its respective factor. Some factors for different ions ar shown in Table 4.2.

Ion	$\mathrm{mg/L}$	$\mathrm{meq/L}$
Na ⁺	$2,2*10^{-5}$	$5 * 10^{-4}$
Ca^{2+}	$5*10^{-5}$	$1*10^{-3}$
Mg^{2+}	$8,2*10^{-5}$	$1 * 10^{-3}$
Cl^-	$1,4*10^{-5}$	$5*10^{-4}$
$\mathrm{SO}_4^{\ 2-}$	$2,1*10^{-5}$	$1 * 10^{-3}$
HCO_3^{-}	$0,8*10^{-5}$	$5*10^{-4}$

Table 4.2: Factors for converting Ion Concentration to Ionic Strength

To apply the equation 4.14 is necessary to consider the molar concentration and the ion charge.



Figure 4.5: CaCO₃ K_{sp} vs Temperature. $\blacksquare = 80$ °C - 176 °F, $\bullet = 50$ °C - 122 °F and $\blacktriangle = 25$ °C. - 77 °F

The results obtained from Equation 4.13 proposed by Taheri *et al.* [35] to find the calcium carbonate K_{sp} as function of T, P and I are shown in figure 4.5. It shows the way that pressure affects the calcium carbonate scaling process.

According to Plummer *et al.* [58], there are several equations for calcium carbonate polymorphisms. The equation that represents the K_{sp} for calcite, aragonite and vaterire are shown in Equation 4.15, 4.16 and 4.17 respectively:

$$logK_{sp} = -171,9065 - 0,077993 * T + \frac{2839,319}{T} + 71,595 * logT$$
(4.15)

$$logK_{sp} = -171,9773 - 0,077993 * T + \frac{2903,293}{T} + 71,595 * logT$$
(4.16)

$$logK_{sp} = -172, 1295 - 0, 077993 * T + \frac{3074,688}{T} + 71,595 * logT$$
(4.17)



Figure 4.6: CaCO₃ K_{sp} vs Temperature. \blacksquare = Calcite, • = Aragonite and \blacktriangle = Vaterite.

The results obtained from Equations 4.15, 4.16 and 4.17 to find the K_{sp} calcium carbonate polymorphisms as function of temperature are shown in figure 4.6.

Considering the pre-salt conditions, the wells are under a huge pressure, even though this situation changes when production begins. Fluids initially are under a higher pressure which decrease while the fluids get far from bottom hole. Using the method proposed by Taheri *et al.* [35] is possible to say that $CaCO_3 K_{sp}$ increase proportionally with pressure. It means that with bigger pressure the solubility and the quantity of dissolved $CaCO_3$ are also bigger, and of course precipitates a lower quantity.

The saturation limit to dissolve some ions decreases when pressure drops which increases the $CaCO_3$ deposition. Critical deposition zones correspond to some points with bigger deposition incidence due to pressure drop are wellhead or close to safety values.

All this issues are caused by the effect that pressure has over the chemical equilibrium of calcium carbonate reaction involve in production petroleum operations.

4.4.2 Saturation Ratio and Saturation Index

Saturation Ratio is a number used to describe the saturation state of a solution. For calcium carbonate, SR is described in Equation 4.18.

$$SR = \frac{[Ca^{2+}][CO_3^{2-}]}{Ksp}$$
(4.18)

The SI is directly bounded with the solution saturation. In chemistry, when the Ksp is higher than salts concentration, the solution is saturated. That is why the limits for SR are the next ones:

SR > 1 Over saturated.

SR = 1 Equilibrium.

SR < 1 Under saturated.

SI is used to describe quantitatively the possibility of occurring a calcium carbonate scaling. It has great importance in petroleum industry as use real parameters to show the possibility of calcium carbonate scaling problems inside the well, pipelines and other equipments with enough anticipation to consider a solution or control method.

There are some researches having the SI as main character to describe the calcium carbonate solutions. It is common using solution properties as salt concentrations, ionic force, temperature, pressure, solution pH among others.

Some methods to describe the solution saturation and the scaling possibility are shown next:

Langelier Saturation Index

LSI is a number that describes the calcium carbonate saturation in a water solution. If it will precipitate or it will dissolved in equilibrium in the aqueous system. LSI is expressed as the difference between the saturation pH and de solution pH measured in the system.

$$LSI = pH - pH_s \tag{4.19}$$

Meanwhile the pH is measured directly in the solution, the pH_s has to be calculated empirically. Langelier proposed an equations system with important variables as $[HCO_3^{-7}]$, $[CO_3^{2-7}]$, $[Ca^+]$ ions concentration in solution. They are shown in Equations 4.20 to 4.24.

$$pH_s = (9,3+A+B) - (C+D) \tag{4.20}$$

$$A = \frac{(\log TDS - 1)}{10} \tag{4.21}$$

$$B = -13, 12\log T(K) + 34, 55 \tag{4.22}$$

$$C = \log_{10}([Ca^{2+}]) - 0, 4 \tag{4.23}$$

$$D = \log_{10}([HCO_3^-/CO_3^{2-}]) \tag{4.24}$$

The LSI is interpreted as follow:

LSI > 0 Over saturated solution, tends to CaCO₃ deposition.

LSI = 0 Saturated solution in equilibrium state.

LSI < 0 Under saturated solution, tends to dissolve CaCO₃.

Stiff&Davis Saturation Index

SI is a variation for LSI, using similar parameters. In order to find the pH_s value were used some graphic methods and a new equations system.

Equation 4.25 represents the pH_s .

$$pH_s = pCa + pAlk + K \tag{4.25}$$

$$SI = pH - pH_s \tag{4.26}$$

SI can be re-written as:

$$SI = pH - pCa - pAlk - K \tag{4.27}$$

With the SI equation proposed by Stiff&Davis is possible to predict the calcium carbonate formation taking into account the constant K, Ca²⁺ and HCO₃⁻ ions concentrations and some others.

K as a function of T and I

As said before, K depends of I and T. Chilingar *et al.* [5], presented the Figure 4.7 to find the constant K as a function of solution properties I and T, it is based on experimental results.



TOTAL IONIC STRENGTH

Figure 4.7: Determination of K as function of T and I [5]



Figure 4.8: Determination of K Using data from [5]



Figure 4.9: Determination of pCa and pAlk from concentrations of Ca^{2+} or $[HCO_3^-+CO_3^{2-}]$ [5]

He also presented the Figure 4.9 to determine the pCa and pAlk values. These are dependents of Ca²⁺ and HCO₃⁻ ions concentrations.



Figure 4.10: Determination of pCa and pAlk from concentrations of Ca^{2+} and $HCO_3^{-} + CO_3^{2-}$. $\Box = Ca$ and $\Delta = Alk$

With Figure 4.7 and 4.9 is possible to find K, pCa and pAlk values to use in the equation 4.25 and get the pH_s value.

The method proposed by Stiff&Davis considers the effects that dissolved CO_2 has in the water to determine the solution pH. It is considered the R' ratio which refers to the CO_2 water interaction.

$$R' = \frac{[HCO_3^-] * 0.82}{x_{CO_2} * S_f} \tag{4.28}$$

In order to calculate R', is necessary to know the S_f value. It depends of the temperature and pressure conditions and can be approximated with Figure 4.11 that considers experimental data:



Figure 4.11: Variation of ${\rm S_f}$ with temperature and pressure [5].

With the value of S_f obtained from Figure 4.11 is possible to calculate the value of R' from equation 4.28. Then is possible to use it in Figure 4.12.



Figure 4.12: Retaltionship between pH and R' value [5]

Finally, with the solution pH and the pH_s is possible to know the SI using Equation 4.26 and predict the saturation state of the solution and finally the possibility of calcium carbonate scaling. The levels to measure the SI effects are similar to LSI's.

Ryznar Stability Index

RSI was designed using an empirical data base of scaling thickness in water systems. It is based on the saturation concept so Ryznar try to relate the calcium carbonate saturation state with the scaling process. The model proposed is shown in Equation 4.29:

$$RSI = 2pH_s - pH \tag{4.29}$$

The levels proposed for RSI are next:

 $RSI \ll 6$ The scaling tendency increases as RSI decreases.

 $RSI \gg 7$ Calcium carbonate formation directed to a corrosion protector layer.

 $RSI \gg 8$ Corrosion problem becomes important.

4.5 Quantitative Methods

Using thermodynamical and kinetics methods is possible to quantify the calcium carbonate scaling process. For this is important to acknowledge the conditions in the system as temperature, pressure and ions concentration.

When kinetics is used to describe the chemical reaction is possible to quantify the Deposition Rate value. It shows the quantity of calcium carbonate on time could be formed under certain conditions of temperature and initial ion concentration.

As temperature dependent, the Deposition Rate could be used as an indirect measure to include another thermodynamic studios such as Fouling Resistance on pipe systems which use the heat transfer theory to estimate the effects of calcium carbonate scaling process.

Now is presented a deeper explanation of quantitative methods for scaling processes.

4.5.1 Deposition Rate

Several authors have made models to quantify the Deposition Rate, this empirical models are based on experimental methods. They allow to study the behavior of calcium carbonate scaling and the driving mechanism.

The model presented by Andristos *et al.* [7] developed by Hasson *et al.* [59] is shown in Equation 4.30:

$$\frac{d\dot{m}}{dt} = \dot{m} = \rho * k_f \frac{dR_f}{dt} \tag{4.30}$$

Deposition rate is considered based on the kinetics. In this way the model presented in Equation 4.31 can be used to evaluate the deposition rate.

$$\dot{m} = K_r * [Ca^{2+}][CO_3^{2-}] - K_{sp}$$
(4.31)

With the equation 4.31 and having the fluid characteristics is possible to relate the chemical parameters with de mass transfer coefficient, Equation 4.33, crystallization coefficient, Equation 4.34, diffusivity, ion concentrations and the flow parameters like Reynolds and Schmidt numbers.

$$\dot{m} = \frac{k_D}{2} \left(x + s + \frac{k_D}{k_R}\right) \left\{1 - \sqrt{1 - \frac{xs - K_{sp}}{\frac{1}{4}(x + s + \frac{k_D}{k_R})^2}}\right\}$$
(4.32)

$$k_D = 0,023USC^{-\frac{2}{3}}Re^{-0.17} \tag{4.33}$$

$$lnk_R = 41,04 - \frac{10417,7}{T_i} \tag{4.34}$$

In this way is possible to find the deposition rate value for the designed solutions under particular system conditions of temperature, pressure, flow velocity, etc.

Quan *et al.* [6] also presented a new method based in Hasson *et al.* [59], it is also a ionic diffusion controlled model, it was expressed as:

$$\dot{m}_c = \frac{k_D [Ca^{2+}]}{2a} (-b + \sqrt{b^2 - 4ac}) \tag{4.35}$$

where

$$a = 1 - \frac{4K_2k_R}{K_1k_D}[Ca^{2+}] \tag{4.36}$$

$$b = \frac{4K_2k_R}{K_1k_D}[HCO_3^-] + \frac{K_{sp}k_R}{k_D}\frac{1}{Ca^{2+}} + \frac{[CO_2]}{[Ca^{2+}]}$$
(4.37)

$$c = \frac{K_{sp}k_R}{k_D} \frac{[CO_2]}{[Ca^{2+2}} - \frac{K_2k_R}{K_1k_D} \frac{[HCO_3^-]^2}{[Ca^{2+2}]}$$
(4.38)

 \dot{m}_c is mass deposition rate per surface, K_1 and K_2 are the first and second proton dissociation constants, K_{sp} the solubility product of calcium carbonate of the solution.

 k_D is the mass transfer coefficient defined previously in Equation 4.33, which considers the effects of fluid properties and conditions as velocity, Reynolds and Schmidt numbers, Equation 4.39 and 4.40 respectively.

$$Re = Ud/v \tag{4.39}$$

$$Sc = v/D \tag{4.40}$$

These numbers considered fluid properties as kinematic and dynamic viscosity also the diffusion of calcium carbonate solution, Equation 4.41

$$D = 3,07 * 10^{-15} \frac{T_b}{\mu} \tag{4.41}$$

Finally, the model take into account the crystallization rate, Equation 4.34, which depends of the temperature of fouling surface.

Both models are based on Hasson *et al.* [59]. The equation presents the CO_3^{2-} ion concentration as participant of the calculation but make the clearance that it is present in solution with high, over 10, solution *pH*, and the concentration of ion HCO_3^- can be used for calculate the mass deposition rate for solution *pH* around 8. Even both methods are based in Hasson's, there is a slight difference when the CO_2 generated is considered in the second method used by Quan *et al.* [6]. Both

methods are diffusion controlled methods so this is why they have similar coefficients.

The quantitative methods presented do not consider the effect that surface could have over the deposition rate. These methods only considers pipe characteristics as diameter having into account that they are diffusion controlled which means they are more affected by the initial concentration rather than scaling surface.

4.5.2 Dynamic Tube Blocking Test

This method is used to study the efficiency of chemical inhibitors to fight or to control the formation and deposition of scales such as calcium carbonate, barium sulphate, strontium sulphate and calcium sulphate. Essentially the TBT look for the time the system gets blocked by scaling process having particular conditions.

The main experimental parameters for the TBT method are the pipe geometry, diameter and length, the ion concentration of the scaling brine, flow regime for brine injection and solution temperature.

In this test two brines with different ions, like Ca^{2+} and HCO_3^{-} are heated inside the pipes submerged in a thermal bath, this two brines mixed in the testing loop with a previously fixed diameter and length where the scaling process is driven.

When scale crystals form inside the testing loop and adhere to the pipe wall cause a differential pressure across the pipe. This difference is monitored to obtain comparative results for the scaling tendency according to the parameters used in the test.

The TBT method allows to analyze the quantity of calcium carbonate scaling remains inside the pipe. Fos this study has to be consider the effective area where the scaling is located taking into account characteristics as pipe diameter, effective length, among others.

Even the scaling process is affected by the available area as it is believed happens forming layer over layer of scaling, in this test has to be consider that the loop get blocked due to the initial solution concentration effect. Also these methods do not considers the effect that scaling by secondary nucleation could have in the deposition rate.

Chapter 5

Methodology

This dissertation focuses on the calcium carbonate scaling using designed brines under conditions of temperature and pressure previously known and controlled through the process. In order to fulfill the objectives were designed and performed some experimental tests besides the use of analytical theories presented in previous studies.

Using the analytical models proposed by Langelier, Stiff&Davis and Ryznar was set an experimental method to predict numerically the values of *LSI*, *SI* and *RSI* for different systems, solution concentration and conditions.

5.1 Experimental Settings

To evaluate the LSI, SI and RSI is necessary to know the solution pH. For that reason was proposed an experimental method that allows to control the temperature and initial conditions for ions concentration responsible of I.

5.1.1 Deposition Solutions Design

Calcium carbonate reaction was used to design the most convenient deposition solutions. A wide concentration range was considered to have low and high concentrations solutions aiming the influence of initial concentration for a successful *SI* analysis.

The main characteristics of compounds used to prepare the deposition solutions are shown in Table 5.1.

Compound	Sodium Bicarbonate	Calcium Chloryde Dihydrate	Acetic Acid
Formula	NaHCO_3	$\rm CaCl_2\cdot 2H_2O$	CH ₃ COOH
CAS	144-55-8	10035-04-8	64-19-7
Molecular Weight [g/mol]	84,01	147,01	$60,\!05$
Purity	99,7	99%	99,70%
Supplied by	VETEC	VETEC	ISOFAR

Table 5.1: Compounds used to prepare the brines with Ca^{2+} and HCO_3^{-} ions.

Table 5.2 shows the salt concentrations of the brines. The brines were prepared at atmospheric pressure and a 22 $\,^{\circ}C$ Temperature.

In order to improve the calcium carbonate formation, for these tests were used a 20% ion calcium excess over the bicarbonate ion.

The HCO_3^- brines were prepared individually for every run, the Ca²⁺ brines were prepared from a stock solution with a 50.000 [ppm] concentration. Stock solution was prepared with $\text{CaCl}_2 \cdot 2 \text{ H}_2\text{O}$ dissolved in deionized water and vacuum filtered with a 0,45 μ m millipore membrane to remove impurities. Deionized water was obtained with the Milli-Q Equipment.

5.1.2 Experimental pH Determination

An experimental setting to measure the solution pH for each test was proposed. In this way there is no need to use graphic methods to calculate the solution pH. The accuracy with this procedure measuring experimental data helps to understand process involved in the calcium carbonate scaling phenomena.

In Figure 5.1 is shown the experimental setting to measure in real time the evolution of the calcium carbonate scaling and the solution pH.

1	START				
2	Phase	Phase 1: Initial 00:00:05 – Completed 03:34:52 – Duration 03:34:47			
		+	★ √C →		E
Stirr [F	Rrpm]	Cool/H	eat to [°C]	Wait [D	D:MM:SS]
4	100	3	5	5	00:43:02
, .		6	10	7	00:17:46
		8	20	9	00:25:17
		10	25	11	00:13:57
		12	30	13	00:17:32
		14	40	15	00:14:31
		16	50	17	00:17:28
		18	60	19	00:16:10
		20	70	21	00:13:36
		22	80	23	00:17:29
		24	90	25	00:16:47
26			END		
26	0	26	20	26	0

Figure 5.1: Experimental Setting ${\rm CaCO}_3$ Deposition

EasyMax Equipment shown in Figure 5.2 and its software, located in the NQTR Laboratory, was used to perform the experimental tests. It works like a batch reactor where is possible to control the solution temperature, stirring and also the time for the test considering some stops to measure the conditions properly trough steps.



Figure 5.2: EasyMax and pH-Meter SevenMulti used for scaling tests: 1: pH-Sensor , 2: Stirrer, 3: pH-Meter SevenMulti, 4: EasyMax Equipment, 5: Software.

Each test was run with a previous known brines containing Ca^{2+} and HCO_3^{-} ions described in Table 5.2.

In Figure 5.1 are listed steps and actions that were taken. For example, the step 6 goal is to achieve 10 °C temperature and it has a wait of 17 minutes and 46 seconds to get a stable and constant temperature till the next step, 8 which its goal is 15 °C, in that way till get a 90 °C temperature.

pH measurements were taken with a SevenMulti pH-Meter and software that is run with the EasyMax software as well so it is able to measure the solution pH in real time as temperature is increasing and calcium carbonate is forming. The pH-Meter transmits the pH value to the EasyMax software data base.

Then, when obtained the experimental data from the software, solution pH measurement was considered when the Temperature was stabilized.

Every test began with 40 mL of HCO_3^- solution at normal conditions, it were cooled till reach 5 °C for about 10 minutes. Then 40 mL of Ca²⁺ were added and the calcium carbonate having the precipitation process started. The final volume of the system was about 80 mL, it means that the real ions concentration decays to half on each brine. The stirring was set at 100 rpm.

In this way was possible to know the solution pH and how it is related to the calcium carbonate precipitation.

5.1.3 pH_s Determination



Figure 5.3: Graphic Tool for SI determination.

In Figure 5.3 is shown the process used to find the SI value. This graphic tool is based in the Stiff&Davis method.

In Section 4.4.2 were described the theoretical methods to find the saturation pH. Using the equations and graphic tools proposed by Langelier [43] and Stiff&Davis [44] was possible to find out the pH_s value having into account the solution properties and conditions, as ionic force, temperature and equilibrium constant. Finally, with pH and pH_s values to know the calcium carbonate saturation state for designed solutions was possible.

5.1.4 Chemical Equilibrium Test

Considering the effects that pH has over the chemical reaction equilibrium and calcium carbonate precipitation itself, it is important to understand both processes. As known, the chemical equilibrium plays an important role in the calcium carbonate deposition. It controls what kind of ion, CO_3^{2-} or HCO_3^{-} is available or

in a bigger quantity in the solution as shown in Figure 4.3.

In order to do that a new group of solutions and the same analysis of pH and temperature were considered. The temperature of the blank solutions was increased from 5 to 90 as explained. The pH behavior was taken into account and compared with the calcium carbonate deposition solutions obtained.

The blank solutions were designed to predict the effects pH has on the $\mathrm{CO_3}^{2^-}/\mathrm{HCO_3}^-$ equilibrium in dependence of temperature with and without consideration of the Ca^{2+} solution addition which produce the calcium carbonate scaling.

The blank solutions characteristics with the desired concentration and the weight of compound needed are shown in Table 5.3. The brines were prepared at atmospheric pressure and a 22 °C temperature.

Table 5.3:
$$\operatorname{CO_3}^{2^-}/\operatorname{HCO_3}^{-}$$
 Equilibrium - Blank Solutions

$$\begin{vmatrix} \operatorname{HCO_3}^{-} \\ [ppm] \\ \operatorname{NaHCO_3} \\ [g] \end{vmatrix} = 0,0028 \ 0,0055 \ 0,0277 \ 0,222 \ 0,415 \end{vmatrix}$$

5.2 Quantitative Analysis

Besides the qualitative study based on analytical methods as Saturation Index there was also the opportunity to present and use a quantitative one that aims to find the amount of $CaCO_3$ may deposits in pipe systems. It was used a different approach to quantify the $CaCO_3$ scaling in pipes.

5.2.1 Deposition Rate

Using parameters such as flow rate, solution composition and geometry of the system the methods presented in Section 4.5.1 were evaluated. The experimental data needed by the methods was obtained from the experimental setting established for the numerical analysis as the solution composition. Other properties like flow regime [20] and molecular diffusion data were taken from previous studies.

Both models use similar information to describe the mass deposition rate. Coefficients like crystallization rate and mass transfer are dependents of the brine composition and temperature system. To calculate this numbers the information provided in Table 5.4 was used, which contains a variety of composition cases previously used in the analytical study.

As said before, some other properties to describe the flow regime were obtained from another experimental studies with similar characteristics to this dissertation. The flow velocity were approximated using the experimental procedure from the Tube Blocking Test considering the pipe geometry and volumetric flow rate used which is shown in Table 5.5

Besides the experimental data is also important the chemical reaction and kinetics properties such as K_1 , K_2 and K_{sp} used for the analysis of the chemical equilibrium of CaCO₃.

Having all the information described was possible to run the models proposed by Quan *et al.* [6] and Andritsos *et al.* [7]. In this way was possible to quantify the mass deposition rate for the composition and condition described in this dissertation and listed in Table 5.4 for solutions composition and Table 5.5 for flow properties.

Table 5.4: Solutions Composition for 5000, 7500 and 10000 [ppm] of $[HCO_3^-]$ initial concentration solution for deposition rate determination.

$[\mathrm{HCO_3}^-] \; [\mathrm{ppm}]$	$[mol/m^3]$			Ι
_	$[\mathrm{HCO}_3^{-}]$	$[\mathrm{Ca}^{2+}]$	$[\mathrm{CO}_2]$	
5000	27,4177	29,2259	13,7088	0,302
7500	41,1265	43,8388	$20,\!5632$	0,453
10000	54,8353	$58,\!4517$	$27,\!4177$	0,604

Table 5.5: Solution Poperties for 5000, 7500 and 10000 [ppm] of $[HCO_3^-]$ initial concentration solution.

Density $[kg/m^3]$	Flow Rate $[m/s]$	Diameter [in]	Pressure [psia]
1004	0,109 0,082 0,0545	1/8 1/16	14,7

5.2.2 Tube Blocking Test

TBT method was used to understand the behavior while changing pipe geometry and how this influence the time in which the tube got blocked having a differential pressure as an indicator.

TBT system is made of two pipes fed with ions solutions pumped with two HPLC pumps, one for each solution. The two solutions encounter and mix into the scaling pipe where chemical reaction occurs and the scaling begins. The system also has a sensor which measures the differential pressure between the beginning and the end of the scaling pipe. The differential pressure system has a software to get the data and monitor the scaling process. The temperature of the solutions was controlled with water heated with a thermal bath at a set temperature. Figure 5.4 shows the TBT system.



(a) TBT System - External View

(b) TBT System - Internal View

Figure 5.4: Dynamic Tube Blocking System

For TBT tests two diameters for the scaling loop, 1/8" and 1/16", were considered. Also, the flow rate for each brine were changed as they are shown in Table 5.7 for the Ca²⁺ and HCO₃⁻ solutions respectively, having an approximately 10 mL/min to 5 mL/min flow rate inside the scaling pipe. These flow rates chosen for TBT test were consistent to the presented in previous researches such as [20] attending the flow regime. Temperature was set in 80 °C taken into account that this temperature favor the calcium carbonate deposition following the chemical equilibrium.

The characteristics for the experimental setting are show in Table 5.6.
$\begin{array}{ c c c } HCO_3^{-} \\ [ppm] \end{array}$	3000	4000	5000	7500	10000
$\begin{bmatrix} Ca^{2+} \\ [ppm] \end{bmatrix}$	3600	4800	6000	9000	12000

Table 5.6: Solutions Compositions for TBT Tests

Table 5.7: Flow Rate Conditions			
Flow Rate [ml/min]	HCO_3^- Brine	Ca^{2+} Brine	
3	4,6	5,4	
2	$3,\!45$	$4,\!05$	
1	2,3	2,7	

As information, the solution concentration given in Table 5.6 refers to the initial concentration of each brine. When the experimental test using the TBT system starts the solution concentration vary having into account the flow rate information given in Table 5.7. This is important to calculate the real concentration of each brine when they were mixed.

5.2.3Tube Blocking Test with Mass Gain

It is important to measure which quantity of calcium carbonate stays in the scaling pipe wall, one method to do that is considering the mass gained. At the end of the test run, system is dismantled and the scaling pipe is retired from the system. After having it dried in an oven, the scaling loop was weight in a analytical scale again and the difference with the clean pipe weight corresponds to the calcium carbonate scaling inside the pipe. The oven and the analytical scale used to analyze mass gain can be seen in Figure 5.5



(a) Oven used to dry the scaling loop.

(b) Analytical Scale

Figure 5.5: Oven and Analytical Scale

After measured the final weight, the scaling loop was cleaned up with a solution of acetic acid to remove the scales and considered to a new test.

To analyze the mass gain inside the loop as a function of the solution composition the information given in Table 5.8 for composition and Table 5.7 for flow rate were considered.

Table 5.8: Solutions Compositions for Mass Gain Determination

HCO ₃ ⁻	5000	7500	10000	
Ca^{2+}	6000	9000	12000	
[ppm]		3000	12000	

Considering the results from the analytical methods presented by Quan *et al.* [6] and Andristos *et al.* [7] and the results of the TBT with mass gain to correlate them and analyze the accuracy of both methods was possible.

Chapter 6

Results and Discussion

Deposition solutions aiming to find the best concentration that improves the calcium carbonate scaling were made. Chemical equilibrium to explain the particular behavior around the solution pH with and without presence of calcium carbonate was also considered.

Experimental solutions following the quantities described in Table 5.2 were made. In most of the Figures presented in this dissertation the HCO_3^{-} ion concentration is only shown in the X-axis, but every value has it correspondent of Ca^{2+} ion concentration as shown in Table 5.2.

6.1 Chemical Equilibrium

To explain the calcium carbonate formation, the chemical reaction equilibrium constants were considered. These K are temperature and ionic force dependent as shown in Equations 4.9 and 4.10. In Figure 6.1 are shown the values for K_1 and K_2 considering the properties and conditions established for the system.



Figure 6.1: Empirical K_1 and K_2 Equilibrium Constants

Comparison of the K_1 and K_2 equilibrium constant values from 5 to 90 °C are shown in Figure 6.1. As it can be seen, the value of K_1 is larger than K_2 's. This means that the chemical reaction will prefer to follow the first proton dissociation reaction rather than the second one.

Being K_1 bigger than K_2 also means that the possibility of formation of ion HCO_3^{-} is also bigger than CO_3^{2-} formation. When there is enough HCO_3^{-} , the reaction will follow its curse and will form the CO_3^{2-} that allow the formation and later precipitation of CaCO_3 . This depends on the initial concentration of ions.

When a big amount of HCO_3^{-} is produced, this helps to the second proton dissociation process and producing more CO_3^{2-} which helps calcium carbonate formation and precipitation.

6.1.1 Blank Solutions and Scaling Solutions

The behavior of the chemical reaction depends on the initial concentration of the solutions that contains the Ca^{2+} and HCO_3^{-} ions. To describe this behavior were considered the solutions shown in Table 5.3. Following the procedure presented in Figure 5.1, the Figure 6.2 was obtained.



Figure 6.2: pH for \blacksquare Blank and \bullet Scaling Solutions

In Figure 6.2 are listed the solutions used to explain the behavior of pH when there is scaling and when there is not. Low concentrations as 25 ppm and 50 ppm experience a particular behavior in contrast with high concentrations as 250 and over. When HCO_3^- ion quantity is low the reaction will prefer to maintain it in this state rather than as a CO_3^{2-} ion form. As can be seen in the Figure 6.2 the pH of the 25 ppm solution tends to increase constantly. It means the chemical equilibrium prefers the first proton dissociation reaction and there is no enough calcium carbonate scaling, it always stays in solution. Otherwise the high concentrations solutions, experiences a droop in the pH as result of the calcium carbonate nucleation and later scaling. The difference intensifies as the concentration increases.

This behavior can be explained according to the Figure 4.3 where the $\text{HCO}_3^$ prefers the pH range about 6.2 to 8.3, point 1 and 3 in the Figure 4.3, which is observed also in the lower concentration solutions, in contrast to the high ones which the pH of blank solutions rises close to 9.5 or to the point 2 in the Figure 4.3.

Now, for the scaling tendency, for low concentrations as was explained before, the reaction prefers to maintain the ion HCO_3^{-} existence instead of going to the CO_3^{2-} ion formation, in this process the solutions at first presents a drop in the pH which increases because of the control of the K_1 , this maintains almost all over temperatures tested.

In other case, for high concentrations, the preference of the chemical reaction is to achieve the second proton dissociation which is later controlled by K_2 increasing the $\text{CO}_3^{2^-}$ ion quantity and favoring the calcium carbonate formation. It means the higher the solution concentration the higher the $\text{CO}_3^{2^-}$ ion availability which cause the bigger calcium carbonate precipitation and scaling.

6.2 Saturation Index

Following the theories explained in Section 4.4.2 and the experimental setting from Section 5.1, qualitative methods as LSI, SI and RSI were considered to evaluate the possibility of calcium carbonate scaling.

6.2.1 Experimental pH

pH for every designed solution is shown in Table 5.2. These pH was found following the procedure described in Figure 5.1. Each test was carried on at least three times till have a good correspondence in data base. The obtained results are shown in

Figure 6.3.



(b) Decreasing Concentrations View

Figure 6.3: Determination of Experimental pH. Temperature [5 90] °C

Figure 6.3 shows the solutions pH from different perspective so it is easy to see the behavior while working with low and high concentrated solutions. The data used to make them is shown in Table A.2.

Figure 6.3 shows the influence that temperature and initial concentration, of ions HCO_3^{-} and Ca^{2+} indeed, have on the solution pH value, even though the effect of ions is remarkable bigger than the effect of temperature. It can be seen as the pH decreases with higher concentrations as they allow easier to the calcium carbonate formation and scaling.

A particular effect that can be seen in the Figure 6.3, for low concentration solutions is that the pH suffers quite interest behavior which goes up in contrast to the experienced by the high concentration solutions. As seen clearer in Figure 6.2 it happens for the chemical equilibrium of the calcium carbonate formation solution.

Decreasing solution pH is caused for the calcium carbonate formation and later precipitation. HCO_3^- and H^+ ions react in order to form the CO_3^{2-} ion as seen in Equation 4.5, the liberation of H^+ ion increase the acidity of the solution which decreases the pH. This pH decreasing can be seen in the 6.3 as is more notorious for higher concentrations because of the availability of HCO_3^- ion that reflects the availability of H^+ ion itself.

Temperature effect is more evident when working with medium concentrations, around 500 to 1500 ppm, in this range can be seen how the pH decreases more dramatically than in higher range. As the chemical reaction equilibrium is highly influenced by temperature is possible to think that the transition from HCO_3^{-} ion to CO_3^{2-} ion in faster having higher temperatures. This effect can be corroborated having into account the behavior or the pH surface around 25 °C where the pH decreases slower than around 80 °C.

The values of experimental pH will be used in the processes for LSI, SI and RSI calculation.

6.2.2 Langelier Saturation Index

Using the Equations 4.20 to 4.24 listed in Section 4.4.2, was possible to find the theoretical pH_s value for the considered range of temperature and the HCO_3^- ion initial concentration in solution. Having the pH_s and applying the Equation 4.19 system LSI was found.

Theroretical pH_s

 pH_s refers to the pH of a solution saturated with CaCO₃. Equation 4.20 designed by Langelier considers every compound that is present in the system. As usual, the HCO_3^- and Ca^{2+} solutions concentration were considered as well as the quantity of TDS. When a solution has more ions besides calcium and bicarbonate the value of TDS influence the results. As shown in Equation 4.22, pH_s is also dependent of temperature which can be explained for the influence that T has over the reaction kinetics which affects the quantity of ions dissolved.

Figure 6.4 shows the value of theoretical pH_s . Knowing pH_s is easier to visualize the influence of ion concentration and temperature. Increasing temperature makes decrease pH_s , this is considering just one concentration line. Instead, the behavior of pH_s with solution ions concentrations is the opposite. Low concentrations results in high pH_s values.



(b) High Concentrations View

Figure 6.4: Theoretical pH_s for LSI

Langelier Saturation Index Determination

Finally, having the pH and pH_s values is possible to find LSI using Equation 4.19. As explained in Section 4.4.2 the LSI value express the possibility of calcium carbonate scaling from under to over saturated solutions. Figure 6.5 shows the results for LSI.

As expressed before, solution concentrations and temperature play an important role in the calcium carbonate scaling as the LSI shows it. In the Figure 6.5 can be seen the areas when most possibly scaling may happen. The area for non saturated and non scaling solution is located when low concentrations were considered. The temperature influence the chemical equilibrium and reaction kinetics what can be seen when both T and LSI are increasing.

As expected, the critical area belong to high concentrations and high temperature conditions.

It is evident the LSI behavior for low and high concentrations. When dealing with low concentrations the LSI value decays more dramatically compared with the increasing rate when working with high ones. Actually, it can be seen as the LSIvalues establish below 2, even though the LSI is an indicator and no a quantifier yet. This tendency came from the experimental pH values which suffers great influence by solutions concentration.



(b) High Concentrations View

Figure 6.5: Experimental LSI

6.2.3 Stiff&Davis Saturation Index

Stiff&Davis presented a modified method to calculate the *SI*. It considers besides the typical temperature and solution concentrations, the chemical and kinetic properties involved in the calcium carbonate scaling process.

To accomplish the SI calculation process the procedure described in Section 4.4.2 for theoretical pH_s involving K and I was used, besides the consideration of pCa and pAlk.

Theroretical pH_s

Theoretical pH_s for SI was obtained having into account the values for K using Equation 6.1 whose coefficients are listed in Table 6.1. Also the values for pCaand pAlk obtained whit Equation 6.2 and 6.3. They are dependents of solution conditions like T, I and solutions concentration. Figure 6.6 and Figure 6.7 shows the surface and curve fitting made using empirical data from [5] for K and pCaand pAlk respectively.

The Curve Fitting Tool from the MatLab Software gives the linear model called Poly35. The name is related to the third and fifth order of the T and I variables respectively. The Poly35 is represented in Equation 6.1 and its coefficients are presented in Table 6.1.

$$K(T, I) = p00 + p10T + p01I + p20T^{2} + p11TI + p02I^{2} + p30T^{3} + p21T^{2}I + p12TI^{2} + p03I^{3} + p31T^{3}I + p22T^{2}I^{2} + p13TI^{3} + p04I^{4} + p32T^{3}I^{2} + p23T^{2}I^{3} + p14TI^{4} + p05I^{5}$$

$$(6.1)$$

	J	
	Poly Coefficients	
p00 = 2.589	p30 = -6.104E-7	p13 = -0.001914
p10 = -0.02672	p21 = -0.0005815	p04 = -0.4132
p01 = 3.491	p12 = -0.005464	p32 = -2.73E-7
p20 = 0.0001417	p03 = 1.801	p23 = -3.566E-5
p11 = 0.02433	p31 = 1.07E-6	p14 = 0.0005234
p02 = -3.709	p22 = 0.0002648	p05 = 0.03553

Table 6.1: Polv35 Coefficients

Using the Equation 6.1, the Figure 6.6 was made. It represents the K values for the range of T and I considered in this dissertation. Having the relation of Kas a function was easier to use it for different values of T and ion concentration responsible of I, in this way the calculation of pH_s was also easier.



Figure 6.6: Using data from Poly35

pCa and pAlk Equations.

The values of pCa and pAlk obtained from the Figure 4.9 and shown in Table A.5 to find the best linear equation that represents them was considered. With the Equation 6.2 and 6.3 was possible to find the values for all the ions solutions considered in this dissertation to calculate the pH_s of the systems without using the graphic tool made by Chilingar [5] *et al.* and presented in Figure 4.9.

$$pCa = -0,429ln(Ca^{2+}) + 4,5525$$
(6.2)

$$pAlk = -0,429ln(\text{HCO}_{3}^{-} + \text{CO}_{3}^{2-}) + 4,7325$$
(6.3)

Figure 6.7 represents the values obtained with the Equation 6.2 and 6.3.



Figure 6.7: Determination of pCa and pAlk from concentrations of Ca^{2+} and $HCO_3^- + CO_3^{2-}$. $\Box = Ca$ and $\Delta = Alk$ from [5] and - = Ca and - = Alk using Equation 6.2 and 6.3

Having K, pCa and pAlk values was possible to use the Equation 4.25 and found the value of the pH_s .

Figure 6.8 shows the results for pH_s . As can be seen in it, the values for pH_s using the *SI* theory has similar behavior to the calculated considering the *LSI* method. It shows correspondence between both methods.



(b) High Concentrations View

Figure 6.8: Theoretical pHs for SI

Stiff&Davis Saturation Index Determination

The index established by Stiff&Davis as well as Langelier's is able to predict the calcium carbonate scaling for aqueous solutions under different conditions of temperature and ion concentrations.

Both are designed considering the SR theory which involves the Ksp described in Equation 4.18, this makes them have similar values and limits. Even though considering experimental data the Stiff&Davis method is more sensible to describe the scaling possibility, and also because it is more accurate when considering the kinetics involved. Figure 6.9 shows the results for SI. It was also considered the low concentration and high concentration view for better interpretation of the process.



Figure 6.9: Experimental SI

6.2.4 Ryznar Stability Index

RSI is based in experimental data base for calcium carbonate scaling in water systems. Correspondence was found and modeled with Equation 4.29. It considers the value of pH_s and pH. This values are experimental and can be represented using the theoretical information presented for the previous index, LSI and SI.

Theroretical pH_s

As said before, the value of pH_s for RSI can be represented using the LSI or SI methods. The SI method is considered more accurate due to the properties and conditions used to determine it, this is the reason for its value will be considered in the process to calculate the RSI.

Ryznar Stability Index Determination

Figure 6.10 shows the representation of RSI. The levels considered by this index are different compared with LSI and SI. Even though the behavior for high temperature and high concentrations are similar. The RSI consider the corrosion effect of the calcium carbonate which is present in low concentrations, area where the value of RSI is bigger. Actually, the lower the RSI the most possible the calcium carbonate scaling tendency is, as Figure 6.10 shows.

RSI also consider the area where even there are a scaling problem, for aqueous systems could be consider no significant because can form a protective film.

For medium to high concentrations, starting in 500 ppm, the RSI express the high possibility of calcium carbonate scaling as can be seen in Table A.9, where the values are lower to 6 considering the levels for RSI.

This behavior is similar to expressed by LSI and SI.



(b) High Concentrations view

Figure 6.10: Experimental RSI

The concept of *SI*, *LSI* and *RSI* is to present a number that describes the state of saturation of a solution and the possibility of calcium carbonate scaling may happens. Going forward of these numbers, were also considered the graphic tool given by the mcView system.

The mcView is a software that take images from the calcium carbonate scaling process. For this dissertation was used in order to corroborate the information given by the *SI*, *LSI* and *RSI* in a graphic way. The images were taken with a webcam to the deposition system as an on-line device. The webcam was located in the EasyMax window while the chemical reaction was occurring.

In every image the mcView software analyze its Red, Green and Blue components, then the software made an average of this information giving the Gray Scale. As the chemical reaction produce changes in the solution like formation and precipitation of calcium carbonate crystals, the software is able to analyze the color changes and monitor the reaction is possible.

In the RGB images shown in Figure 6.11 the reaction behavior in real time can be monitored. As a particular information, for example, for low concentration as 25 or 50, shown in Figures 25 and 50, the average has no representative variation as in higher concentration as 1500 or 2000, shown in Figures 1500 and 2000. The 5000 ion concentration shown in Figure 5000, the mcView software is able to describe the moment when crystals are no longer suspended in solution and get together to full precipitation to the bottom of the batch reactor. Is clearly a evidence of the transition from nucleation to crystal formation.



Figure 6.11: Gray Sccale for Scaling Solutions: — Average, — R, — G and —B component

6.3 Deposition Rate

Deposition rate relates scale growth with time and area units so the closest meaning to the deposition rate is how fast the chemical reaction occurs and the scales are formed taken into account several characteristics from the medium, solution or environment.

The methods presented by Quan *et al.* [6] and Andritsos *et al.* [7] were used. As it can be seen in Figure 6.12 both of them present a clear dependency on the initial concentration of the scaling solutions. Even though the difference between both models is evident as well. It is related with the considerations every model has on respect of the reaction kinetics.

The fact that both uses the K_{sp} indicates that consider this interaction has an important play role in the scaling process. But more important, the consideration of chemical equilibrium constants K_1 and K_2 . With these, the model presented by Quan *et al.* [6] is not only an ionic diffusion controlled but also a crystallization by chemical reaction controlled method. It might be considered more accurate with the reality because they considerate the chemical interaction using the equilibrium constants besides the production of CO_2 as it may be seen in the Equation 4.35.

As predicted by the chemical equilibrium and kinetics models presented before, the calcium carbonate scaling process is driven by the amount of compounds and also proportional to the solution temperature. As much as the temperature and composition increase, it affects the deposition rate value.

Initially a variety of temperatures going from 5 to 90 °C, a constant flow velocity of 0,109 m/s and some concentrated solutions with Ca^{2+} and HCO_3^{-} ions were considered. For a better understanding, the solution concentration shown in Figure 6.12 is corresponding with the initial concentration of the HCO_3^{-} ions solution; having into account the influence of the flow rate this concentration may vary when mixed with the Ca^{2+} ions solution, the relation of the concentration is shown in Table B.1 Results are shown in Figure 6.12.

In Figure 6.12 are shown the effect that temperature an solution concentration have over the deposition rate.



(a) Mass Deposition Rate by Quan - Flow Rate 1 (b) Mass Deposition Rate by Andritsos - Flow Rate 1



(c) Mass Deposition Rate by Quan - Flow Rate 2 (d) Mass Deposition Rate by Andritsos - Flow



(e) Mass Deposition Rate by Quan - Flow Rate 3 (f) Mass Deposition Rate by Andritsos - Flow Rate 3

Figure 6.12: Mass Deposition Rate using Hasson Ionic Diffusion Model. $\blacksquare = 5.000$, • = 7.500 and $\blacktriangle = 10.000 \text{ [ppm] of [HCO_3^-] initial concentration solution.}$

To improve the understanding of the scaling process and the effect that changes in the flow rate have over the deposition rate the Figure 6.13 was considered. In this Figure were considered the flow rate used in the experimental tests and a constant temperature of 80 °C. It is possible to see how an increasing in the flow rate also causes an increasing in the deposition rate.





Figure 6.13: Mass Deposition Rate using Hasson Ionic Diffusion Model. \blacksquare = Flow Rate 1, • = Flow Rate 2 and \blacktriangle = Flow Rate 3 of [HCO₃⁻] at 80 °C.

6.4 Tube Blocking Test

TBT system was used to analyze the influence of the geometry, changing tube diameter and the influence of flow rate variation over the time the TBT system get blocked by calcium carbonate scaling. With the results obtained was possible to establish the better range of solutions concentration to evaluate the quantity of calcium carbonate scales deposit inside the scaling pipe.

6.4.1 Geometry Influence

The influence that geometry has over the scaling time was analyzed. In order to do this two loops of 1/8" and 1/16" were used.

It is important to say that the TBT was calibrated for the 1/8" pipe. Almost all of the tests run with this pipe, the differential pressure starts between 0 and 60. In these tests was analyzed the time that takes to occur the blocking using a scaling solution of calcium carbonate. When the differential pressure achieves the top of 1200 the tests were stopped to avoid permanent blocking.

Even though the initial differential pressure for the 1/16" pipe starts in about 380 mBar and the one for the 1/8" pipe starts in about 60 mBar, this difference has no big relevance since the final differential pressure will be 1200 mBar for both.

In Figure 6.14 are shown the results using both diameters for a variety of solution concentrations. It is easy to appreciate the general behavior the scaling time has under different geometries. When using the 1/8" diameter loop the scaling time is bigger than using the 1/16" diameter Loop.



Figure 6.14: Influence of Geometry over Scaling Time. $\bullet = 1/16$ " Pipe Diameter and $\blacktriangle = 1/8$ " Pipe Diameter

In the petroleum industry, places with high incidence of fouling or scaling are the ones that have geometry changes as diameter reductions. The results for these tests having a change in the geometry point to the same idea.

6.4.2 Flow Rate Influence

As it was mentioned in Section 5.2.2, the TBT was used to analyze the influence that flow rate has over the scaling time and its response through the differential pressure sensor. The experimental test were carried on using the information from Table 5.6 for the concentration solutions and Table 5.7 for the variety of flow rates used.

In Figure 6.15 are shown the results for scaling time when varying the flow rate. There is sufficient evidence to say that the flow rate is indirectly proportional to scaling time, it means that having a bigger flow rate cause a shorter scaling time in the experimental tests. There is not a linear relation between flow rate and scaling time.



Figure 6.15: Influence of Flow Rate over Scaling Time \blacksquare = Flow Rate 1, • = Flow Rate 2 and \blacktriangle = Flow Rate 3 and Experimental Mass Gain using TBT System

The influence that flow rate has over the scaling time could be explained based on the theory that the calcium carbonate scaling has a diffusion driven mechanism where ion concentration plays an important role. When having a bigger flow rate, there is also a bigger amount of calcium carbonate nucleus increasing the possibility of them coming together which eventually will cause the scaling in pipe walls. As it can be seen in Figure 6.15, the bigger the flow rate and the higher the HCO_3^- ion concentration, Ca^{2+} ion concentration indeed, the shorter scaling time was obtained.

6.5 TBT With Experimental Mass Gain

Following the procedure described in Section 5.2.3, to analyze the mass of calcium carbonate scaling in the TBT system a series of experimental tests were run. In Figure 6.16 are shown the results for the solution concentration considered and run in the TBT system.



Figure 6.16: Mass Gain using the TBT System \blacksquare = Flow Rate 1, • = Flow Rate 2 and \blacktriangle = Flow Rate 3 and Experimental Mass Gain using TBT System

In Figure 6.16 can be seen the behavior of the calcium carbonate scaling weighed. The calcium carbonate scaling presents a particular behavior taking into account that is not completely dependent nor affected by the flow rate. If something can be said about the mass gained of calcium carbonate is that it increases with the initial concentration solution. Is evident that when having a higher amount of calcium and bicarbonate ions in the solutions there is more calcium carbonate production.

As the analytical methods proposed by Quan *et al.* [6] and Andritsos *et al.* [7] give a quantity of deposited mass over area and time, those models were taken into account to compare their results with the experimental results obtained with the TBT system, they are shown in Figure 6.17. The scaling time that takes to every solution to block the TBT system was taken into account among with the quantity of deposited mass in the system. In this way was possible to relate both analytical and experimental results.



(a) Mass Gain by Quan et al. [6] and Experimental Mass Gain using TBT



(b) Mass Gain by Andritsos et al. [7] and Experimental Mass Gain using TBT

Figure 6.17: Mass Gain using Quan *et al.* [6] and Andritsos *et al.* [7] Ionic Diffusion Model. \blacksquare = Flow Rate 1, • = Flow Rate 2 and \blacktriangle = Flow Rate 3 and Experimental Mass Gain usin TBT System \Box = Flow Rate 1, • = Flow Rate 2 and \triangle = Flow Rate 3

According to Figure 6.17, experimental test and analytical methods can be

related. Both models, Quan *et al.* [6] and Andritsos *et al.* [7] have considerably lower results of quantity of calcium carbonate scales.

Correspondence between the results for Quan *et al.* [6] and Andritsos *et al.* [7] can be explained having into account the average of time got by the TBT system to be blocked. When having a higher flow rate, the average deposition time is lower when having a lower flow rate, this can be seen in Figure 6.15. But, considering the relation between the scaling time and flow rate, the product for each case is similar.

Considering the confidence interval for TBT with experimental mass deposition tests and the analytical results can be seen a coincidence between both results. The reason Andritsos *et al.* [7] method is closer to the experimental results could be due to the method considerations themselves. Andritsos *et al.* [7] method consider the influence of calcium and bicarbonate ions only while Quan *et al.* [6] consider the influence of produced dioxide carbonate as well.

A difference between Quan *et al.* [6] and Andritsos *et al.* [7] methods yields in the consideration of K_1 and K_2 equilibrium constants. This consideration was taken by Quan *et al.* [6] only. It implies that Quan *et al.* [6] method considers the influence that bicarbonate/carbonate ions have over the calcium carbonate formation. According to information presented before, this influence plays an important role.

Chapter 7

LTS Loop Design

Using analytical and experimental results shown in Chapter 6 is possible to project a new loop to operate in the Subsea of Technology Laboratory, LTS. The LTS Loop will be designed to handle the best conditions to assure the calcium carbonate scaling in the wall pipes.

As seen before, the Saturation Index is an important measure to describe a scaling system. Properties as solution pH and ionic force depends on the ions present in the solution. This was the premise to star doing tests to analyze the solution pH in the NQTR Laboratory as it will behave in similar way independent of the volume of the solutions, of course keeping the same initial concentration.

7.1 Methodology

LTS Loop design is based on chemical reaction and kinetics theories around the calcium carbonate formation, among with the study using the NQTR Loop about geometric changes and mass gain.

To find and assure the best solution composition was used the Saturation Index theories, and to analyze the deposition rate and mass gain were used the Quan and Andristos methods taking into account the geometric characteristics for the LTS Loop, also changes in flow rate were considered.

7.1.1 Experimental Setting

Main characteristics for LTS Loop are shown in Table 7.1.

Table 7.1: Solutions Compositions for Mass Gain Determination in the LTS Loop

HCO_3^-	5.000	7.500	10.000
[ppm]	0.000		10.000
Ca^{2+}	6 000	0 000	12 000
[ppm]	0.000	5.000	12.000

The initial concentration solution considered for the LTS Loop were based on the experimental test run in the NQTR Laboratory. The possibility of having a wide interval of concentration makes it more convenient to analyze the limits of the systems and the influence of each property as well.

Having a complete analysis and control of the scaling system is crucial and very important to work properly. Pressure and temperature sensors along the LTS Loop System and a pH-Meter are important to data acquisition during the tests. These sensors will be strategically located as shown in Figure 7.1, which is an initial configuration for the LTS Loop.

The solution temperature will be set at 80 °C and the scaling zone will be heated with a thermal tape to maintain the temperature and induce the calcium carbonate scaling in there.

The LTS Loop was thought to work as a batch reactor as the solution will no leave the system, it means the crystals will continually circulate through the pipes till have a blockage or stop the test in a pre determined time, actually in this way will be possible to generate a calcium carbonate deposition on time curve. The solution will be under continue stirring to avoid scaling in the solution tank a.k.a Batch Reactor.

The scaling will be analysed using removable body tests, which is a piece of pipe that can be removed from the system when a particular test is over. It has the same characteristics as the pipes and a length of 15 mm. Table 7.2 shows a better description of the body test.

Measure	[mm]
Outside Diameter	$33,\!3$
Schedule	$3,\!05$
Nominal Size	27,2
Length	15

Table 7.2: Body Test Characteristics

The body test will be located before and after the magnetic conditioning zone in the LTS Loop. In this section will be analysed the influence external devices have on the calcium carbonate scaling process. As it can be inferred, the before magnetic zone test will be serve as a blank to compare with the after one.



Figure 7.1: LTS Loop System

7.1.2 Deposition Rate

For LTS Loop Deposition Rate analysis will be consider the empirical models proposed by Quan *et al.* [6] and Andristos *et al.* [7], the were described in Section 4.5.1 and used for NQTR Loop system in Section 6.3 having particular considerations such as geometry, flow rate, temperature and solutions composition.

The main considerations for LTS Loop will be a constant temperature of 80 °C. Based on experimental test the solutions compositions will be similar to presented in Table 5.8 for NQTR Loop system.

A big change will be the LTS Loop geometry, principally the diameter considered for this project is about 1". The flow rate close to 0,9 m/s used for the NQTR Loop system will be re sized properly to allow comparisons for flow regime with previous studies.

Solution properties as kinematic and dynamic viscosity, ionic diffusion values will be considered the same for the NQTR system taking into account is the same aqueous solution and temperature.

In Figure 7.2 are shown the results for mass of calcium carbonate scaling considering the methods proposed by Quan and Andritsos. The characteristics of the fluid and geometry of the pipe to be used in the LTS Loop were considered.

There is a limit line representing the top of calcium carbonate scaling possible under determinate conditions and time. This limit was calculated taking into account the total volume of the body test described in Table 7.2 where is possible to accumulate the calcium carbonate scaling and also considering the density of the aragonite polymorphism which is the most probable with the temperature system considered.

As it can be seen in the Figure 7.2, considering the top and bottom initial concentration solution this mass limit marks a time that goes from around 9 hours to 18 hours and from around 4,5 hours to 9 hours using the Quan and Andritsos method respectively. This times allow to plan a series of experimental test to be performed in the LTS Loop having the time as a parameter to stop the tests.



(b) Prediction of Mass Gain using Andritsos Model

Figure 7.2: Prediction of Mass Gain using Quan and Andritsos Ionic Diffusion Model for $\blacksquare = 5.000$ [ppm], $\bullet = 7.500$ [ppm], $\blacktriangle = 10.000$ [ppm] of HCO3- Initial Concentration Solution and - - Mass Deposition Limit

Chapter 8

Conclusions and Recommendations for Future Research

8.1 Conclusions

- Scaling is a frequent problem in the oil and gas industry. It mostly occurs under supersaturation of salts causing troubles from down hole, along the pipelines and inside process equipment. The determination of scaling characteristics as saturation index have become the first analysis in order to describe its severity. The results for the saturation indexes used in this dissertation show an important accuracy with the designed experimental tests.
- Different conditions of solution temperature and initial concentration were tested, each of them takes to different and particular results. The influence of each condition was evaluated showing as a big game changing the variation from low to high concentration. The possibility of control the initial concentration allowed to choose the best candidates to upcoming researches.
- There is a remarkable relation between the solution pH and the calcium carbonate scaling process. At first this relation was studied in order to use the saturation index methods, later, taking into account its particular behavior for under saturated to supersaturated solutions was possible to add knowledge to the scaling process in regard to the chemical equilibrium presented between bicarbonate and carbonate ions.

- It was probed using experimental tests run in the NQTR Laboratory the negative influence that increasing flow rate cause in the scaling time. Increasing the flow rate causes a lower scaling time. Nevertheless the experimental tests were maintained in linear regime, this information helps to set convenient flow rate for future experiments.
- The influence of different pipe diameter was analyzed, showing a positive influence over the scaling time as well. Using a bigger pipe diameter causes a bigger scaling time. This incidence has been portrayed before, and it has been the explanation for the equipments that are more alike to suffer scaling problems. To sustain this was also used the saturation ratio concept which increase in particular equipments or geometry changing places.
- Analytical models to predict the calcium carbonate scaling process were used. The influence of the initial concentration of the solutions used to run the models through the experimental test under similar conditions was confirmed. Although, there is a difference between the experimental and analytical results for calcium carbonate mass deposited in the wall pipe.
- In general, the properties analyzed such as geometry, flow rate, initial concentration is related and indicative of a mass transfer process which is indeed in the analytical models that were studied. The effect each of these characteristics was statistically analyzed having the conclusion that the bigger the diameter the longer the deposition time, the bigger the flow rate the shorter the deposition time which is similar when analyzing concentration solutions. Therefore, the flow rate presents a bigger negative effect over the deposition time when compared with varying concentration.
- The idea of performing mass gain experiments using a dynamic system was considered. Even though the results presents a wide confidence interval, this takes to think that controlling the deposition process is still a long but possible ride. Therefore, the solution concentrations presented a positive influence giving understanding that when having higher concentration the scaling time drops but the amount of calcium carbonate scaling rises corresponding to the mass transfer theory as well.
- This dissertation provides new understanding and knowledge to the calcium carbonate scaling process in order to future research opening the possibility
of using the presented methodology surrounding the mass gain tests in bigger structures in the oil and gas industry.

- The influence that flow rate has over the deposition time was analyzed with analytical methods having that the bigger the flow rate the higher the flow rate which is consistent with the experimental results showing that the bigger the flow rate, the shorter the scaling time due to there is more scales formed so the tube gets blocked faster.
- To find a true solve for scaling problems is unrealistic, but adding information and scientific knowledge regard to the scaling process may help to a brighter future.
- The analytical models used in this dissertation can describe the scaling process and certainly the can be used as predictive methods as they are related with the experimental test. The difference between the results for experimental and analytical methods can be explained for the considerations they have with properties as initial concentration, calcium carbonate diffusivity and crystal density as all of them are empirical.
- Tanking into account the analytical and experimental results, even the Quan *et al.* ?? method is the less related this takes consideration of the CO_2 production which makes it more related to the chemical process and ions presented in the solution.

8.2 Recommendations for Future Research

- First, as a continuance for this dissertation, the implementation of the methodology described in Section 7 considering a real size pipe dynamic system.
- A wider interval of flow rate and geometry is recommended in order to a better understanding of their influence over the scaling process.

- Taking advantage that calcium carbonate polymorphisms can be controlled with temperature is possible to analyze their influence over the deposition time or mass gain processes.
- Particular methods as presented in this dissertation can be used or adapted considering some other scales such as sulphates, also the possibility of co-deposition processes, which results as a new road to follow.
- Whenever there is a good control over the deposition process the doors will be open for new research not just considering physical methods to correct the scaling problems but to proof mostly used chemical inhibitors in real size pipe systems.

Bibliography

- MIKE CRABTREE, DAVID ESLINGER, P. F. M. M. A. J., KING, G., Fighting Scale - Removal and Prevention, Tech. rep., Oilfield Review, 1999.
- [2] Available in http://www.luminoruv.com/education_softening.php, Dezember 2015.
- [3] TAKESHI OGINO, T. S., SAWADA, K., "The Formation and Transformation Mechanism Of Calcium Carbonate in Water", Geochimica et Cosmochimica Acta, 1987.
- [4] Available in http://www2.warwick.ac.uk/fac/sci/chemistry/research/ mrodger/mrodgergroup/group/present/msrgbk/research/caco3/, Dezember 2015.
- [5] GEORGE V. CHILINGAR, R. M., AL-QAHTANI, G. D., The Fundamentals of Corrosion and Scaling for Petroleum and Environmental Engineers. Guls Publishing Company, 2008.
- [6] QUAN ZHENHUA, C. Y., CHONGFANG, M., "Experimental Study of Fouling on Heat Transfer Surface During Forced Convective Heat Transfer", *Chinese Journal of Chemical Engineering*, 2008.
- [7] N. ANDRITSOS, A. J. K., KOUTSOUKOS, P., "Calcium Carbonate Deposit Formation under Isothermal Conditions", *The Canadian Journal Of Chemical Engineering*, 1996.
- [8] CRABTREE, M., E. D. F. P. M. M. J. A. K. G., "Oilfield", 1999.
- [9] ANP, "Boletim da Producao de Petroleo e Gas Natural", 2014.
- [10] R. L. C. BELTRAO, C. L. SOMBRA, A. C. V. M. L. J. F. N., HENRIQUES, C. C. D., "Challenges and New Technologies For The Development Of The Pre-Salt Cluster, Santos Basin, Brazil". In: Offshore Technology Conference, 2009.

- [11] ESEOSA, A., ATUBOKIKI, A. J., "Prediction and Monitoring of Oilfield Carbonate Scales using Scale Check(c)", Society of Petroleum Engineers, 2011.
- [12] DE ANDRADE LIMA, D., Quantificacao De Fases Cristalinas De Incrustacoes Em Colunas De Producao De Petroleo Pelo Metodo Rietveld, Master's Thesis, Universidade Federal Do Rio Grande Do Norte, 2010.
- [13] CIVAN, F., "Reservoir Formation Damage: Fundamentals, Modeling Assessment and Mitigation", Gulf Publishing Company - Houston Texas, 2000.
- [14] LARSON, T. E., BUSWELL, A. M., Calcium Carbonate Saturation Index And Alkalinity Interpretations, Tech. rep., Department of Registration and Education - State Water Survey Division, 1943.
- [15] DAVID HASSON, MORDECAI AVRIEL, W. R. T. R., WINDREICH, S., Mechanism of Calcium Carbonate Scale Deposition on Heat-Transfer Surfaces, Master's Thesis, Department of Chemical Engineering, Technion Israel Institute of Technology, 1968.
- [16] NANCOLLAS, G. H., SAWADA, K., "Formation Of Scales Of Calcium Carbonate Polymorphs: The Influence Of Magnesium Ion and Inhibitors", *Society of Petroleum Engineers*, 1982.
- [17] PRZYBYLINSKI, J. L., "The Role Of Bicarbonate Ion In Calcite Scale Formation", Society of Petroleum Engineers - Production Engineering, 1987.
- [18] ODDO, J. E., TOMSON, M. B., "A New Saturation Index Equation To Predict Calcite Formation In Gas And Oil Production", Society of Petroleum Engineers, 1991.
- [19] ODDO, J. E., TOMSON, M. B., "Why Scales Form And How To Predict It", Society of Petroleum Engineers - Production and Facilities, 1994.
- [20] M. SULTHAN KHAN, S. M. ZUBAIR, M. O. B. A. K. S. A. Q., "Fouling resistance model for prediction of CaCO₃ scaling in AISI 316 tubes", *Heat* and Mass Transfer, 1996.
- [21] ASHLEY JOHNSON, D. E., LARSEN, H., "An Abrasive Jetting Scale Removal System", Society of Petroleum Engineers, 1998.

- [22] RAYMOND JASINSKI, K. T., SABRENOLLE, W., "Calcite Scaling Tendencies For North Sea HPHT Wells: Prediction, Authentication and Application", Society of Petroleum Engineers, 1998.
- [23] M. O. BUDAIR, M. SULTHAN KHAN, S. M. Z. A. K. S., QUDDUS, A., "CaCO₃ scaling in AISI 316 stainless steel tubes - effect of thermal and hydraulic parameters on the induction time and growth rate." *Heat and Mass Transfer*, 1998.
- [24] POLIZZOTTI, L. A. P. D. M., "Scale Control In Thermal Desalination Processes", *Corrosion*, 1999.
- [25] ZHANG, Y., FARQUHAR, R., "Laboratory Determination of Calcium Carbonate Scaling Rates For Oilfield Wellbore Environments." Society of Petroleum Engineers, 2001.
- [26] FERGUSON, R. J., "Predicting Calcium Oxalate Scale", Corrosion, 2002.
- [27] MARIA C. M. BEZERRA, FRANCISCA F. ROSARIO, A. A. R., "Scale Prediction and Remediation for Deep Water Fields", Society of Petroleum Engineers, 2002.
- [28] J. MOGHADASI, H. MULLER-STEINHAGEN, M. R. I., MOTAIE, E., "Scale Formation In Iranian Oil Reservoir And Production Equipment", Society of Petroleum Engineers, 2003.
- [29] BOUDREAUX, C., FALK, K., "A Unified Approach For The Removal Of Barium Sulfate Scale Using Coiled Tubing", Society of Petroleum Engineers, 2005.
- [30] KARI RAMSTAD, TRINE TYDAL, K. M. A., FOTLAND, P., "Predicting Carbonate Scale In Oil Producers From High-Temperature Reservoirs", *Society of Petroleum Engineers*, 2005.
- [31] TAO CHEN, A. N., YUAN, M., "Calcium Carbonate Scale Formation assessing the initial stages of precipitation and deposition." *Journal of Petroleum Science & Engineering*, 2005.
- [32] CAVANO, R. R., "Understanding Scaling Indices And Calculating Inhibitor Dosages", Corrosion, 2005.
- [33] H. J. SHIPLEY, A. T. KAN, G. F. D. S., TOMSON, M. B., "Effect of Hydrate Inhibitors on Calcite, SSulfate and Halite Formation", *Society* of Petroleum Engineers, 2006.

- [34] FATHI ALIMI, MOHAMED TLILI, M. B. A. C. G., MAURIN, G., "Influence of magnetic field on calcium carbonate precipitation." *Desalination*, 2007.
- [35] A. TAHERI, R. MASOUDI, M. Z., ATAEI, A. R., "Simulation and Experimental tudies of Mineral Scale Formation Effect on Performance of an Iranian Carbonate Oil Reservoir Under Water Injection." Society of Petroleum Engineers, 2008.
- [36] TORE LARSEN, PREBEN RANDHOL, M. L. L. O. J., OSTVOLD, T., "Kinetics of CaCO₃ Scale Formation During Core Flooding", Society of Petroleum Engineers, 2008.
- [37] W. M. AL NASSER, A. A. SHAIKH, M. J. H., SALMAN, A. D., "Determining Calcium Carbonate Scale Kinetics by Online Technique", *Particulate Systems Analysis*, 2008.
- [38] MASON TOMSON, CHUNFANG FAN, H. L. P. Z. H. A., KAN, A. T., "Integration of Kinetics into Scale Prediction Software, ScaleSoftPitzer", *Society of Petroleum Engineers*, 2009.
- [39] SENTHILMURUGAN, B., GHOSH, B., "Low Molecular Weight Co-Polymer for Calcium Scale Inhibition at High Temperature", Society of Petroleum Engineers, 2009.
- [40] GUAN, H., "Carbonate Scaling Prediction: The importance of Valid Data Imput", Corrosion, 2010.
- [41] HAIPING LU, A. T. K., TOMSON, M. B., "Effect of Monoethylene Glycol on Carbonate Equilibrium and Calcite Solubility in Gas/Monoethylene Glycol/NaCL/Water Mixed Systems", Society of Petroleum Engineers, 2010.
- [42] BAHADORI, A., "Estimation of Potencial Precipitation From an Equilibrated Calcium Carbonate Aqueous Phase Using Simple Predictive Tool", SPE Projects, Facilities & Construction, 2011.
- [43] LANGELIER, W. G., "The Analytical Control of Anti-Corrosion Water Treatment", Journal American Water Works Association, 1936.
- [44] HENRY A. SITT, J., DAVIS, L. E., "A Method For Predicting The Tendency Of Oil Field WWater To Deposit Calcium Carbonate", *Petroleum Transactions*, AIME, 1952.

- [45] NAN ZHANG, AMY KAN, W. S. H. A. S. A. M. B. T., "A Novel Approach to the Study of CaCO3 Precipitation Kinetics on Carbon Steel Pipe", *Society of Petroleum Engineers*, 2012.
- [46] XUAN LIU, TAO CHEN, P. C. H. M. T. H. B. W. X. Y., "Understanding the Co-deposition of Calcium Sulphante and Barium Sulphate and Developing Environmental Acceptable Scale Inhibitors Applied in HTHP Wells." Society of Petroleum Engineers, 2012.
- [47] JING, G., LI, X., "Dynamic Laboratory Research on Synergistic Scale Inhibition Effect of Composite Scale Inhibitor and Efficient Electromagnetic Anti-Scaling Instrument", *Research Journal of Applied Sciences*, 2013.
- [48] MAVREDAKI, E., NEVILLE, A., "Prediction and Evaluation of Calcium Carbonate Deposition SUrfaces", Society of Petroleum Engineers, 2014.
- [49] T. M. PAAKKONEN, M. RIIHIMAKI, C. J. S. E. M., KEISKI, R. L., "Modelling CaCO₃ crystallization fouling on heat exchanger surface - Definition of fouling layer properties and model parameters." *International Journal of Heat and Mass Transfer*, 2015.
- [50] WIGG, H., FLETCHER, M., "Establishing the True Cost of Downhole Scale Control." International Conference on Oilfield Scaling, 1995.
- [51] JORDAN, M. M., C. I. R., MACKAY, E. J., "Low Sulfate Seawater Injection for Barium Sulfate Scale Control: A Life-of-Field Solution to a Complex Challenge." Society of Petroleum Engineers, 2008.
- [52] C. A. FRANCO, J. R. SOLARES, H. M. A.-M. A. E. M. N. H. R., SAIHATI, A. H., "Analysis of Deposition Mechanism of Mineral Scales Precipitating in the Sandface and Production Strings of Gas-Condensate Wells." *Society* of Petroleum Engineers, 2010.
- [53] A. SAIFELNASR, M. BAKHEIT, K. K., LILA, A., "Calcium Carbonate Scale Formation, Prediction and Treatment (Case Study Gumry Oilfield-PDOC)", International Letters of Chemistry, Physics and Astronomy, 2013.
- [54] CELSO APARECIDO BERTRAN, CLAUDIO MARCOS ZIGLIO, F. S. D.-W. L., "Cinetica de Formacao de Incrustacoes de CaCO3 e BaSO4 e o efeito de Inibidores. O uso de Microbalanca de Quartzo (QCM) como detector." Sociedade Brasileira de Quimica.

- [55] Available in http://www.mindat.org/min-859.html, November 2015.
- [56] Available in http://www.mindat.org/min-307.html, November 2015.
- [57] Available in http://www.mindat.org/min-4161.html, November 2015.
- [58] PLUMMER, L. N., BUSENBERG, E., "The solubilities of calcite, aragonite and vaterite in CO₂-H₂O ssolution between) and 90 C, and an evaluation of the aqueous model for the system CaCO₃-CO₂-H₂O", *Geochimica et Cosmochimica Acta*, v. 46, pp. 1011–1040, 1982.
- [59] HASSON D., S. H., M., B., "Prediction of calcium carbonate scaling rates." In: Proceedings og 6th International Symposium Fresh Water from the Sea, 1978.

Appendix A

Analytical and Experimental Results

A.1 Chemical Equilibrium

	HCO_{3}^{-} [ppm]		TEMPERATURE									
		5	10	20	25	30	40	50	60	70	80	90
						SOLU	IOITI	N pH				
BLANK	25	7,86	7,84	7,86	7,90	$7,\!94$	8,02	8,15	8,29	8,42	8,58	8,75
	50	$7,\!90$	$7,\!92$	$7,\!96$	8,01	8,08	8,14	8,26	8,38	8,48	8,64	8,83
	250	8,75	8,71	8,68	8,68	8,68	8,69	$8,\!74$	8,84	$8,\!97$	$9,\!16$	$9,\!32$
	2.000	8,72	8,72	8,72	8,72	$8,\!74$	8,78	8,85	8,96	$9,\!10$	$9,\!30$	$9,\!48$
	3.750	8,67	8,66	8,65	8,65	8,65	8,67	8,71	8,78	8,85	$8,\!95$	$9,\!06$
SCALING	25	$7,\!79$	$7,\!75$	$7,\!70$	$7,\!71$	$7,\!74$	7,77	$7,\!85$	$7,\!96$	8,09	8,28	8,51
	50	8,04	8,00	$7,\!95$	$7,\!94$	$7,\!96$	$7,\!97$	8,03	8,13	8,24	8,40	8,46
	250	8,36	8,32	8,19	8,13	8,07	$7,\!98$	$7,\!85$	$7,\!69$	$7,\!50$	$7,\!31$	$7,\!17$
	2.000	$6,\!83$	$6,\!62$	$6,\!40$	$6,\!28$	$6,\!19$	$6,\!04$	$5,\!92$	$5,\!84$	$5,\!79$	5,77	$5,\!88$
	3.750	6,40	$6,\!27$	$6,\!11$	$6,\!07$	$6,\!04$	$5,\!99$	$5,\!98$	$5,\!96$	$5,\!94$	$5,\!95$	$6,\!02$

 Table A.1: Chemical Equilibrium - Blank vs Scaling Solutions

A.2 Experimental pH

HCO_3^{-} [ppm]	TEMPERATURE [°C]										
	5	10	20	25	30	40	50	60	70	80	90
				EX	PERI	MEN	TAL	pH			
25	7,86	7,82	7,78	7,79	7,81	7,84	7,90	8,01	8,14	8,31	8,4
	$7,\!79$	$7,\!74$	7,70	$7,\!71$	$7,\!73$	$7,\!76$	$7,\!84$	$7,\!95$	8,08	8,26	8,4
	$7,\!73$	$7,\!68$	$7,\!63$	$7,\!64$	$7,\!67$	7,70	$7,\!80$	$7,\!92$	8,05	8,27	8,6
50	8,19	8,16	8,12	8,11	8,12	8,12	8,18	8,29	8,38	8,49	8,4
	8,08	8,01	$7,\!95$	$7,\!94$	$7,\!94$	$7,\!95$	8,00	8,09	8,20	8,40	8,4
	$7,\!86$	$7,\!82$	$7,\!78$	$7,\!79$	$7,\!81$	$7,\!84$	$7,\!90$	8,01	8,14	8,31	8,4
125	8,16	8,12	8,08	8,08	8,09	8,09	8,12	8,15	8,12	$7,\!99$	7,7
	8,24	8,22	8,18	8,18	8,19	8,20	8,25	8,30	8,32	8,12	7,8
	8,36	8,33	8,29	8,27	8,26	8,25	8,26	8,23	8,04	$7,\!71$	7,5
250	8,57	8,54	8,48	8,45	8,42	8,34	8,21	8,04	$7,\!84$	$7,\!61$	7,4
	8,21	8,19	8,15	8,15	8,14	8,10	8,02	$7,\!89$	7,70	$7,\!47$	7,2
	8,31	8,23	$7,\!93$	$7,\!79$	$7,\!66$	$7,\!49$	$7,\!32$	$7,\!15$	$6,\!97$	$6,\!83$	6,8
500	8,44	8,38	8,25	8,15	8,03	$7,\!86$	$7,\!65$	$7,\!44$	$7,\!24$	$7,\!03$	6,9
	8,15	8,10	$7,\!98$	$7,\!88$	$7,\!76$	$7,\!57$	$7,\!38$	$7,\!19$	$7,\!03$	$6,\!90$	$6,\!8$
	$7,\!68$	$7,\!59$	$7,\!38$	$7,\!23$	$7,\!09$	$6,\!93$	$6,\!75$	$6,\!57$	$6,\!42$	$6,\!49$	6,1
1.000	$7,\!73$	$7,\!44$	$7,\!14$	$7,\!00$	$6,\!89$	$6,\!71$	$6,\!52$	$6,\!34$	$6,\!22$	$6,\!14$	6,1
	$7,\!80$	$7,\!61$	$7,\!34$	$7,\!20$	$7,\!07$	$6,\!89$	$6,\!67$	$6,\!45$	$6,\!29$	$6,\!12$	6,1
	$7,\!31$	$7,\!02$	$6,\!73$	$6,\!60$	$6,\!48$	$6,\!32$	$6,\!14$	$5,\!98$	$5,\!84$	$5,\!78$	5,8
1.500	$7,\!07$	$6,\!84$	$6,\!65$	$6,\!55$	$6,\!44$	$6,\!31$	$6,\!22$	$6,\!19$	$6,\!20$	6,21	6,2
	$7,\!21$	$6,\!96$	$6,\!73$	$6,\!61$	$6,\!48$	$6,\!29$	$6,\!12$	$5,\!99$	$5,\!92$	5,87	5,8
	$6,\!77$	$6,\!53$	$6,\!32$	$6,\!20$	$6,\!08$	$5,\!92$	$5,\!80$	5,71	5,67	$5,\!68$	5,7
2.000	$7,\!04$	$6,\!82$	$6,\!60$	$6,\!49$	$6,\!39$	$6,\!24$	$6,\!14$	$6,\!06$	6,00	$5,\!97$	6,0
	$6,\!93$	6,70	$6,\!46$	$6,\!34$	$6,\!23$	$6,\!07$	$5,\!93$	$5,\!83$	5,77	5,73	5,7
	$6,\!52$	$6,\!33$	$6,\!14$	$6,\!03$	$5,\!94$	$5,\!80$	$5,\!69$	$5,\!64$	$5,\!60$	$5,\!60$	5,7
2500	$6,\!94$	6,72	$6,\!49$	$6,\!40$	$6,\!33$	$6,\!24$	$6,\!16$	$6,\!10$	$6,\!05$	$6,\!04$	6,1
	6,90	$6,\!69$	$6,\!51$	$6,\!44$	$6,\!39$	$6,\!31$	$6,\!27$	$6,\!24$	$6,\!18$	$6,\!14$	6,2
	$6,\!95$	6,74	$6,\!42$	$6,\!34$	$6,\!18$	$6,\!02$	$5,\!84$	5,74	$5,\!69$	$5,\!69$	5,6
3.750	$6,\!38$	$6,\!29$	$6,\!16$	$6,\!13$	$6,\!11$	$6,\!05$	$6,\!01$	$5,\!95$	$5,\!91$	$5,\!89$	5,9
	$6,\!25$	$6,\!11$	$5,\!97$	$5,\!95$	$5,\!93$	$5,\!88$	$5,\!92$	$6,\!01$	$6,\!03$	$6,\!05$	6,1
	$6,\!58$	$6,\!42$	$_{6,21}$	$6,\!13$	$6,\!08$	$6,\!02$	6,00	$5,\!94$	$5,\!89$	$5,\!89$	$5,\!9$
5.000	$6,\!04$	$5,\!98$	$5,\!94$	$5,\!94$	$5,\!94$	$5,\!90$	$5,\!90$	$5,\!88$	$5,\!83$	$5,\!83$	5,9
	$7,\!24$	$5,\!93$	$5,\!74$	5,71	5,71	$5,\!68$	$5,\!69$	5,70	$5,\!68$	5,67	5,7
	$5,\!95$	$5,\!88$	5,74	5,71	$5,\!69$	$5,\!63$	$5,\!62$	$5,\!61$	$5,\!61$	$5,\!62$	5,6

Table A.2: Experimental pH of Designed Chemical Solutions

A.3 Theoretical pH_s

A.3.1 Theoretical $pH_s LSI$

Table A.3: Theoretical pH_s using LSI Equations													
HCO_{3}^{-} [ppm]			TE	MPE	RATU	JRE[°C]					
	5	10	20	25	30	40	50	60	70	80	90		
		Theoretical $pH_s LSI$											
25	9,42	9,32	9,12	9,02	8,93	8,75	8,57	8,39	8,22	8,06	7,90		
50	8,85	8,75	8,55	8,45	8,36	8,17	$7,\!99$	$7,\!82$	$7,\!65$	$7,\!49$	$7,\!33$		
125	8,09	$7,\!99$	7,79	7,70	$7,\!60$	$7,\!42$	$7,\!24$	7,06	6,90	6,73	$6,\!57$		
250	$7,\!52$	$7,\!42$	$7,\!22$	$7,\!12$	$7,\!03$	$6,\!85$	$6,\!67$	$6,\!49$	$6,\!32$	$6,\!16$	6,00		
500	$6,\!95$	$6,\!85$	$6,\!65$	$6,\!55$	$6,\!46$	$6,\!27$	6,09	$5,\!92$	5,75	$5,\!59$	$5,\!43$		
1.000	$6,\!38$	6,28	6,08	$5,\!98$	$5,\!89$	5,70	$5,\!52$	$5,\!35$	$5,\!18$	$5,\!02$	4,86		
1.500	6,04	$5,\!94$	5,74	$5,\!65$	$5,\!55$	$5,\!37$	$5,\!19$	$5,\!01$	4,85	4,68	4,52		
2.000	$5,\!80$	5,70	$5,\!51$	5,41	$5,\!31$	$5,\!13$	4,95	4,78	4,61	4,44	4,29		
2.500	$5,\!62$	$5,\!52$	$5,\!32$	$5,\!22$	$5,\!13$	$4,\!95$	4,77	$4,\!59$	4,42	4,26	4,10		
3.750	$5,\!29$	$5,\!18$	4,99	4,89	4,80	4,61	4,43	4,26	4,09	3,93	3,77		
5.000	$5,\!05$	4,95	4,75	4,65	4,56	4,37	4,19	4,02	3,85	3,69	3,53		

A.3.2 Theoretical pH_s SI

Determination of K

Ι	TEMPERATURE[°C]										
	0	10	20	25	30	40	50	60	70	80	90
						Κ					
0	2,60	2,30	2,18	1,75	1,73	1,70	1,44	1,36	1,20	1,11	0,93
0,2	3,24	$3,\!00$	2,82	2,70	$2,\!59$	2,40	$2,\!21$	$1,\!91$	$1,\!67$	$1,\!38$	$1,\!13$
0,4	$3,\!49$	$3,\!32$	3,16	$3,\!06$	$2,\!96$	2,72	$2,\!56$	$2,\!19$	$1,\!90$	$1,\!58$	$1,\!25$
0,6	$3,\!62$	$3,\!49$	$3,\!34$	$3,\!26$	$3,\!14$	$2,\!91$	$2,\!69$	$2,\!32$	$2,\!03$	$1,\!68$	$1,\!34$
0,8	$3,\!71$	$3,\!59$	$_{3,45}$	$3,\!38$	$3,\!24$	$3,\!01$	$2,\!77$	$2,\!42$	$2,\!11$	$1,\!77$	$1,\!40$
1	$3,\!77$	$3,\!64$	$3,\!51$	$_{3,43}$	$3,\!30$	$3,\!08$	$2,\!81$	$2,\!48$	$2,\!16$	$1,\!81$	$1,\!42$
1,2	$3,\!79$	$3,\!66$	$3,\!53$	$3,\!46$	$3,\!32$	$_{3,12}$	$2,\!84$	$2,\!51$	$2,\!18$	$1,\!83$	$1,\!44$
1,4	$3,\!79$	$3,\!65$	$3,\!54$	$_{3,45}$	$3,\!32$	$_{3,13}$	$2,\!85$	$2,\!51$	$2,\!18$	$1,\!84$	$1,\!43$
$1,\!6$	$3,\!79$	$3,\!64$	$3,\!52$	3,43	$3,\!31$	$_{3,13}$	$2,\!85$	$2,\!50$	$2,\!16$	$1,\!83$	$1,\!42$
1,8	$3,\!76$	$3,\!60$	$_{3,49}$	$_{3,40}$	$3,\!29$	$_{3,10}$	$2,\!83$	$2,\!49$	$2,\!15$	$1,\!81$	$1,\!40$
2	3,72	$3,\!59$	$3,\!46$	$3,\!37$	$3,\!24$	$3,\!06$	$2,\!80$	$2,\!46$	$2,\!12$	$1,\!78$	$1,\!37$
2,2	$3,\!68$	$3,\!54$	3,40	$3,\!30$	$_{3,20}$	$3,\!00$	$2,\!74$	$2,\!41$	$2,\!08$	$1,\!73$	$1,\!32$
2,4	$3,\!63$	$3,\!50$	$3,\!36$	$3,\!26$	$_{3,15}$	$2,\!94$	$2,\!69$	$2,\!37$	$2,\!03$	$1,\!67$	$1,\!27$
2,6	$3,\!59$	$3,\!44$	3,30	$_{3,20}$	$3,\!09$	$2,\!88$	$2,\!62$	$2,\!30$	$1,\!96$	$1,\!60$	$1,\!19$
2,8	$3,\!52$	$3,\!39$	$3,\!24$	3,13	$3,\!02$	$2,\!80$	$2,\!54$	$2,\!24$	$1,\!88$	$1,\!51$	$1,\!10$
3	$3,\!47$	$3,\!33$	$3,\!18$	$3,\!07$	$2,\!94$	$2,\!71$	$2,\!46$	$2,\!16$	$1,\!80$	$1,\!43$	$1,\!01$
3,2	$3,\!40$	$3,\!26$	$_{3,10}$	$2,\!98$	$2,\!88$	$2,\!64$	$2,\!36$	$2,\!06$	$1,\!69$	$1,\!31$	$0,\!89$
3,4	$3,\!31$	$3,\!19$	$3,\!01$	$2,\!90$	$2,\!80$	$2,\!54$	$2,\!26$	$1,\!91$	$1,\!56$	$1,\!14$	0,76
3,6	3,22	3,12	2,92	2,80	2,70	2,42	$2,\!14$	1,78	1,38	$0,\!94$	0,48

Table A.4: Determination of K for various Ionic strenghts - Data from [5]

Determination of pCa and pAlk

$Ca^{2+} \text{ or} HCO_3^{-} + CO_3^{2-}$	pCa	pAlk	pCa Eq. 6.2	pAlk Eq. 6.3
10.000	0,6	0,78	0,60	0,78
4.000	1	1,18	$0,\!99$	$1,\!17$
1.000	$1,\!58$	1,76	$1,\!59$	1,77
400	$1,\!98$	$2,\!16$	$1,\!98$	2,16
100	$2,\!58$	2,76	$2,\!58$	2,76
40	$2,\!97$	$3,\!15$	$2,\!97$	$3,\!15$
10	-	-	$3,\!56$	3,74

Table A.5: Data for determination of pCa and pAlk

A.3.3 Theoretical pH_s SI and RSI

	Ta	ble A	.6: T	heore	tical j	pH_s u	sing	SI Me	thod		
HCO_{3}^{-}				TE	MPE	RATU	JRE[°C]			
	5	10	20	25	30	40	50	60	70	80	90
				1	$pH_s S$	I and	RSI				
25	9,50	9,38	9,15	9,04	8,94	8,75	8,57	8,41	8,25	8,09	7,93
50	8,91	8,79	8,56	8,45	8,35	8,16	$7,\!98$	$7,\!81$	$7,\!65$	$7,\!49$	7,33
125	8,13	8,01	7,78	$7,\!67$	$7,\!57$	$7,\!38$	$7,\!20$	$7,\!04$	$6,\!87$	6,71	$6,\!55$
250	$7,\!55$	$7,\!43$	$7,\!20$	$7,\!10$	$6,\!99$	6,80	$6,\!62$	$6,\!45$	$6,\!29$	$6,\!13$	$5,\!97$
500	6,99	$6,\!87$	$6,\!64$	$6,\!53$	$6,\!43$	$6,\!24$	$6,\!06$	$5,\!89$	5,72	$5,\!55$	$5,\!39$
1.000	$6,\!45$	$6,\!33$	$6,\!10$	6,00	$5,\!90$	5,70	$5,\!52$	$5,\!34$	$5,\!17$	4,99	4,82
1.500	$6,\!16$	$6,\!04$	$5,\!82$	5,71	$5,\!61$	$5,\!41$	$5,\!22$	$5,\!04$	4,86	4,68	$4,\!50$
2.000	$5,\!97$	$5,\!85$	$5,\!62$	$5,\!52$	$5,\!42$	$5,\!22$	$5,\!03$	4,84	4,66	$4,\!47$	4,28
2.500	$5,\!83$	5,71	$5,\!49$	$5,\!38$	$5,\!28$	$5,\!08$	4,88	4,69	$4,\!50$	4,31	$4,\!11$
3.750	$5,\!60$	$5,\!49$	$5,\!27$	$5,\!16$	$5,\!06$	4,85	$4,\!65$	$4,\!45$	$4,\!25$	$4,\!04$	3,82
5.000	$5,\!46$	$5,\!35$	$5,\!14$	$5,\!03$	4,93	4,72	4,51	4,30	4,08	3,86	$3,\!62$

A.4 Saturation Index

A.4.1 LSI

			r	Table .	A.7: L	SI					
$\mathrm{HCO_3}^- \; \mathrm{[ppm]}$				ΤE	MPEI	RATU	RE[°C	C]			
	5	10	20	25	30	40	50	60	70	80	90
						LSI					
25	-1,63	-1,57	-1,42	-1,31	-1,19	-0,98	-0,72	-0,43	-0,13	0,22	0,60
50	-0,79	-0,74	-0,59	-0,50	-0,40	-0,20	$0,\!03$	$0,\!29$	$0,\!55$	0,80	$0,\!89$
125	$0,\!21$	0,28	$0,\!43$	$0,\!53$	$0,\!63$	0,80	$0,\!99$	$1,\!16$	$1,\!28$	$1,\!29$	$1,\!23$
250	$0,\!87$	$0,\!95$	$1,\!10$	$1,\!17$	$1,\!25$	$1,\!37$	$1,\!45$	$1,\!47$	$1,\!45$	$1,\!38$	$1,\!36$
500	$1,\!14$	$1,\!18$	$1,\!22$	1,20	$1,\!17$	$1,\!18$	$1,\!17$	$1,\!15$	$1,\!15$	$1,\!22$	$1,\!20$
1.000	$1,\!19$	$1,\!01$	$0,\!93$	0,89	$0,\!87$	0,88	$0,\!87$	0,86	$0,\!89$	$0,\!94$	$1,\!11$
1.500	$0,\!97$	$0,\!84$	$0,\!82$	0,80	0,78	0,81	0,86	$0,\!95$	$1,\!09$	$1,\!24$	$1,\!44$
2.000	$1,\!03$	0,92	$0,\!89$	$0,\!87$	$0,\!87$	$0,\!91$	$0,\!97$	1,06	$1,\!19$	$1,\!32$	$1,\!59$
2.500	$1,\!31$	1,20	$1,\!15$	$1,\!17$	$1,\!17$	1,24	1,32	$1,\!43$	$1,\!55$	1,70	$1,\!86$
3.750	$1,\!12$	$1,\!09$	$1,\!13$	1,18	$1,\!24$	$1,\!38$	$1,\!55$	1,71	$1,\!86$	$2,\!02$	$2,\!25$
5.000	$1,\!36$	$0,\!98$	$1,\!06$	$1,\!13$	$1,\!22$	$1,\!36$	$1,\!54$	$1,\!71$	1,86	2,02	2,24

				Table	A.8: \$	SI					
$\mathrm{HCO_3}^- \; [\mathrm{ppm}]$				TE	MPEI	RATU	RE[°C	C]			
	5	10	20	25	30	40	50	60	70	80	90
						SI					
25	-1,71	-1,63	-1,45	-1,33	-1,20	-0,98	-0,73	-0,45	-0,16	0,19	0,58
50	-0,87	-0,79	-0,61	-0,51	-0,39	-0,19	$0,\!05$	$0,\!31$	$0,\!59$	0,90	$1,\!13$
125	$0,\!12$	0,21	$0,\!40$	$0,\!50$	$0,\!61$	0,80	$1,\!00$	$1,\!19$	$1,\!29$	$1,\!23$	$1,\!15$
250	$0,\!81$	$0,\!89$	$0,\!99$	$1,\!03$	$1,\!08$	$1,\!17$	$1,\!22$	$1,\!24$	$1,\!21$	$1,\!18$	$1,\!21$
500	$1,\!10$	$1,\!16$	$1,\!23$	$1,\!22$	$1,\!20$	$1,\!22$	$1,\!21$	$1,\!18$	$1,\!18$	$1,\!25$	$1,\!25$
1.000	$1,\!16$	$1,\!02$	$0,\!97$	$0,\!94$	$0,\!92$	$0,\!94$	$0,\!93$	$0,\!92$	$0,\!95$	$1,\!02$	$1,\!21$
1.500	0,86	0,74	0,75	0,74	0,73	0,76	0,82	0,92	$1,\!07$	$1,\!24$	$1,\!46$
2.000	0,86	0,77	0,77	0,76	0,77	0,82	$0,\!89$	$1,\!00$	$1,\!14$	1,30	$1,\!60$
2.500	$1,\!11$	$1,\!01$	$0,\!99$	$1,\!01$	$1,\!02$	$1,\!11$	1,21	$1,\!33$	$1,\!47$	$1,\!65$	1,86
3.750	0,80	0,79	$0,\!85$	0,90	0,98	$1,\!13$	$1,\!33$	$1,\!51$	1,70	1,91	2,20
5.000	$0,\!94$	$0,\!57$	$0,\!67$	0,75	$0,\!85$	$1,\!02$	$1,\!22$	$1,\!43$	$1,\!63$	$1,\!85$	$2,\!15$

A.4.3 RSI

			Ta	ble A.	<u>9: RSI</u>						
HCO_{3}^{-} [ppm]				TEM	PERA	TUR	E[°C]				
	5	10	20	25	30	40	50	60	70	80	90
					LS	SI					
25	11,21	11,01	10,60	10,37	10,15	9,73	9,30	8,85	8,40	7,90	7,35
50	9,76	9,56	$9,\!16$	8,95	8,74	8,34	7,94	$7,\!51$	$7,\!10$	6,70	$6,\!45$
125	$7,\!96$	7,75	7,34	$7,\!13$	6,92	$6,\!54$	$6,\!18$	$5,\!85$	$5,\!57$	$5,\!40$	$5,\!30$
250	6,72	$6,\!50$	6,09	$5,\!89$	5,71	$5,\!39$	$5,\!13$	$4,\!95$	4,81	4,72	$4,\!57$
500	$5,\!89$	5,71	$5,\!41$	$5,\!31$	$5,\!23$	$5,\!02$	$4,\!85$	4,70	$4,\!54$	4,30	4,14
1.000	$5,\!34$	$5,\!37$	$5,\!20$	$5,\!12$	$5,\!04$	4,82	4,64	$4,\!47$	4,26	4,04	$3,\!67$
1.500	$5,\!30$	$5,\!30$	$5,\!06$	$4,\!97$	4,88	4,64	4,40	$4,\!12$	3,79	$3,\!45$	3,03
2.000	$5,\!10$	$5,\!08$	$4,\!85$	4,75	$4,\!65$	4,39	$4,\!13$	3,84	$3,\!52$	$3,\!17$	$2,\!68$
2.500	4,72	4,70	$4,\!50$	$4,\!37$	$4,\!26$	$3,\!97$	3,68	3,36	$3,\!03$	2,66	$2,\!25$
3.750	4,80	4,70	4,42	4,26	4,08	3,72	3,33	$2,\!94$	$2,\!55$	$2,\!12$	$1,\!61$
5.000	4,52	4,78	$4,\!47$	4,28	4,08	3,70	3,29	$2,\!87$	$2,\!46$	$2,\!01$	$1,\!47$

Appendix B

Deposition Rate

B.1 Solution Concentration Used for Quan and Andritsos Methods

Table B.1: Solution Concentration Used for Quan and Andritsos Methods: Solution Concentration^{*}, Solution Concentration After Mixing^{**} and Molar Concentration After Mixing^{***}

	$[\mathrm{ppm}]^*$	[ppm]**	$[\text{ mol/m}^3]^{***}$
HCO_{3}^{-}	5.000	2.300	$26,\!05$
	7.500	3.450	41,14
	10.000	4.600	55,06
Ca^{2+}	6.000	3.240	29,28
	9.000	4.860	44,04
	12.000	6.480	58,86

B.1.1 K_1, K_2 and K_{sp} Constants

Table B.2: Determination of K_1 , K_2 and K_{sp} from Equations 4.9, 4.10 and 4.12 for $\blacksquare = 5.000$, $\bullet = 7.500$ and $\blacktriangle = 10.000$ [ppm] of $[HCO_3^{-}]$ initial concentration solution.

T [°C]	T [K]	$\mathrm{K_{1}[mol^{2}/L^{2}]}$	$\mathrm{K_{2}[mol^{2}/L^{2}]}$		Ksp	
				5.000	7.500	10.000
5	$278,\!15$	$3,\!05E-07$	2,69E-11	2,20E-07	3,77E-07	$5,\!60E-07$
10	$283,\!15$	$3,\!44\text{E-}07$	3,13E-11	$1,\!89E-07$	$3,\!24\text{E-}07$	$4,\!82E-07$
15	$288,\!15$	$3,\!81E-07$	$3,\!59\text{E-}11$	$1,\!62E-07$	2,78E-07	$4{,}14\text{E-}07$
20	293,15	$4,\!15E-07$	4,05E-11	$1,\!39E-07$	$2,\!38E-07$	3,54E-07
25	298,15	$4,\!45\text{E-}07$	4,51E-11	$1,\!18E-07$	2,03E-07	$3,\!02E-07$
30	303,15	4,70E-07	4,95E-11	1,00E-07	1,72E-07	2,56E-07
35	308,15	4,90E-07	5,37E-11	8,51E-08	1,46E-07	2,17E-07
40	$313,\!15$	$5,\!04\text{E-}07$	5,76E-11	7,18E-08	1,23E-07	$1,\!83E-07$
45	$318,\!15$	$5,\!14\text{E-}07$	6,11E-11	$6,\!05E-08$	$1,\!04\text{E-}07$	1,54E-07
50	323,15	$5,\!18E-07$	6,42E-11	$5,\!07E-08$	8,70E-08	$1,\!29E-07$
55	$328,\!15$	$5,\!17E-07$	6,67E-11	$4,\!24\text{E-}08$	7,28E-08	$1,\!08E-07$
60	$333,\!15$	$5,\!13E-07$	6,88E-11	3,53E-08	6,06E-08	9,02E-08
65	$338,\!15$	$5,\!04\text{E-}07$	7,03E-11	2,94E-08	$5,\!04\text{E-}08$	$7,\!49E-08$
70	$343,\!15$	$4,\!92E-07$	7,12E-11	$2{,}43\text{E-}08$	$4{,}17\text{E-}08$	6,20E-08
75	$348,\!15$	4,76E-07	7,16E-11	2,01E-08	$3,\!44E-08$	$5,\!12\text{E-}08$
80	$353,\!15$	$4,\!59\text{E-}07$	7,15E-11	$1,\!65E-08$	2,83E-08	4,21E-08
90	$363,\!15$	$4,\!19E-07$	6,99E-11	1,11E-08	1,90E-08	2,83E-08

Flow and Molecular Diffusion Parameters **B.1.2**

Tabl	le B.3: .	Flow and M	<u>lolecular</u> I	<u> DIffusion F</u>	aram	eters
T [°C]	T $[K]$	$\mu~[{\rm Kg/ms}]$	$D~[m^2/s]$	$\nu \; [m^2/s]$	Sc	k_R
5	$278,\!15$	2,73E-03	3,12E-10	2,72E-06	8719	36
10	$283,\!15$	2,04E-03	4,26E-10	$2{,}03\text{E-}06$	4781	70
15	$288,\!15$	$1,\!64E-03$	5,39E-10	$1,\!64E-06$	3035	132
20	$293,\!15$	1,38E-03	6,52E-10	$1,\!37E-06$	2109	245
25	$298,\!15$	1,20E-03	7,65E-10	$1,\!19E-06$	1557	445
30	303, 15	1,06E-03	8,78E-10	1,06E-06	1201	792
35	$308,\!15$	9,54E-04	9,92E-10	9,50E-07	958	1384
40	$313,\!15$	8,70E-04	1,10E-09	$8,\!67E-07$	784	2375
45	$318,\!15$	8,02E-04	1,22E-09	$7,\!99E-07$	656	4005
50	323,15	$7,\!45\text{E-}04$	1,33E-09	$7,\!42E-07$	557	6648
55	328,15	6,97E-04	$1,\!44E-09$	6,95E-07	481	10864
60	$333,\!15$	6,57E-04	1,56E-09	6,54E-07	420	17496
65	$338,\!15$	6,21E-04	$1,\!67E-09$	$6,\!19\text{E-}07$	370	27780
70	343,15	$5,\!90\text{E-}04$	1,78E-09	$5,\!88E-07$	330	43520
75	$348,\!15$	$5,\!63E-04$	1,90E-09	$5,\!61E-07$	296	67304
80	$353,\!15$	$5,\!39E-04$	2,01E-09	5,37E-07	267	102810
90	$363,\!15$	4,98E-04	$2{,}24\text{E-}09$	$4{,}96\text{E-}07$	222	231644

Table B.3: Flow and Molecular DIffusion Parameters

T [°C]	Re	k_d	Re	k_d	Re	k_d
	Flo	w Rate 1	Flo	w Rate 2	Flov	w Rate 3
5	28	1,68E-06	42	2,35E-06	56	2,99E-06
10	37	$2{,}39\text{E-}06$	56	$3,\!34E-06$	75	$4,\!24\text{E-}06$
15	47	$3,\!11E-06$	70	$4,\!36\text{E-}06$	93	5,54E-06
20	55	$3,\!85E-06$	83	$5,\!40E-06$	111	$6,\!85E-06$
25	64	$4,\!61E-06$	96	$6,\!45\text{E-}06$	128	8,19E-06
30	72	$5,\!36E-06$	108	7,51E-06	144	9,53E-06
35	80	$6{,}13\text{E-}06$	120	$8{,}58\text{E-}06$	160	$1,\!09E-05$
40	88	$6{,}89\text{E-}06$	132	$9,\!65E-06$	176	1,22E-05
45	95	$7,\!66E-06$	143	$1,\!07E-\!05$	190	1,36E-05
50	102	$8{,}43\text{E-}06$	154	$1,\!18E-\!05$	205	1,50E-05
55	109	$9{,}20\mathrm{E}{-}06$	164	$1{,}29\text{E-}05$	219	$1,\!63E-\!05$
60	116	9,96E-06	174	$1,\!40\text{E-}05$	233	1,77E-05
65	123	$1,\!07E-\!05$	184	$1{,}50\text{E-}05$	246	$1,\!91E-05$
70	129	$1,\!15E-05$	194	$1,\!61E-05$	259	$2{,}04\text{E-}05$
75	136	$1{,}23\text{E-}05$	203	$1{,}72\text{E-}05$	271	$2{,}18\text{E-}05$
80	142	$1{,}30\text{E-}05$	212	$1{,}82\text{E-}05$	283	$2{,}32\text{E-}05$
90	153	$1,\!45\text{E-}05$	230	$2{,}04\text{E-}05$	306	$2{,}59\text{E-}05$

Table B.4: Reynolds Number and Mass Transfer Coefficient

B.1.3 Determination of a, b and c parameters from Equations 4.36, 4.37 and 4.38.

Table B.5: Determination of a, b and c parameters from Equations 4.36 , 4.37 and 4.38 for 5.000, 7.500 and 10.000 [ppm] of $[\text{HCO}_3^{-}]$ initial concentration solution using Flow Rate 1 = 0.0545 m/s.

T [°C]	a	b	с	a	b	с	a	b	с
		5.000			7.500			10.000	
5	-2,2E+05	2,0E+05	-4,4E+04	-3,3E+05	3,1E+05	-7,3E+04	-4,5E+05	4,2E+05	-9,8E+04
10	-3,1E+05	$2,\!8E\!+\!05$	-6,2E+04	-4,7E+05	$4,\!4E\!+\!05$	-1,0E+05	-6,3E+05	5,9E+05	-1,4E+05
15	-4,7E+05	$4{,}2\mathrm{E}{+}05$	-9,3E+04	-7,1E+05	$6,\!6E\!+\!05$	-1,5E+05	-9,4E+05	$8,8E{+}05$	-2,1E+05
20	-7,3E+05	6,5E+05	-1,4E+05	-1,1E+06	1,0E+06	-2,4E+05	-1,5E+06	$1,\!4E\!+\!06$	-3,2E+05
25	-1,1E+06	1,0E+06	-2,3E+05	-1,7E+06	$1,\!6E\!+\!06$	-3,8E+05	-2,3E+06	2,2E+06	-5,1E+05
30	-1,8E+06	$1,\!6E\!+\!06$	-3,6E+05	-2,7E+06	$2,\!6E\!+\!06$	-6,0E+05	-3,7E+06	$3,\!4E\!+\!06$	-8,0E+05
35	-2,9E+06	$2,\!6E\!+\!06$	-5,7E+05	-4,4E+06	$4,\!1E\!+\!06$	-9,5E+05	-5,8E+06	$5,5E{+}06$	-1,3E+06
40	-4,6E+06	$4,1E{+}06$	-9,1E+05	-6,9E+06	$6,5E{+}06$	-1,5E+06	-9,3E+06	8,7E+06	-2,0E+06
45	-7,3E+06	$6,5E{+}06$	-1,4E+06	-1,1E+07	1,0E+07	-2,4E+06	-1,5E+07	$1,\!4E\!+\!07$	-3,2E+06
50	-1,1E+07	1,0E+07	-2,3E+06	-1,7E+07	$1,\!6E\!+\!07$	-3,8E+06	-2,3E+07	2,2E+07	-5,0E+06
55	-1,8E+07	$1,\!6E\!+\!07$	-3,5E+06	-2,7E+07	2,5E+07	-5,9E+06	-3,6E+07	$3,\!4E\!+\!07$	-7,8E+06
60	-2,8E+07	2,5E+07	-5,5E+06	-4,1E+07	$3,\!9E{+}07$	-9,1E+06	-5,5E+07	5,2E+07	-1,2E+07
65	-4,2E+07	$3,\!8E{+}07$	-8,4E+06	-6,4E+07	$5,9E{+}07$	-1,4E+07	-8,5E+07	$^{8,0E+07}$	-1,9E+07
70	-6,4E+07	5,7E+07	-1,3E+07	-9,7E+07	$9,\!0E\!+\!07$	-2,1E+07	-1,3E+08	1,2E+08	-2,8E+07
75	-9,7E+07	$^{8,6E+07}$	-1,9E+07	-1,5E+08	$1,\!4E\!+\!08$	-3,2E+07	-1,9E+08	1,8E+08	-4,3E+07
80	-1,4E+08	1,3E+08	-2,8E+07	-2,2E+08	2,0E+08	-4,7E+07	-2,9E+08	2,7E+08	-6,3E+07
90	-3,1E+08	2,8E+08	-6,2E+07	-4,7E+08	$4,\!4E\!+\!08$	-1,0E+08	-6,3E+08	$5,9E{+}08$	-1,4E+08

Table B.6: Determination of a, b and c parameters from Equations 4.36 , 4.37 and 4.38 for 5.000, 7.500 and 10.000 [ppm] of $[\text{HCO}_3^-]$ initial concentration solution using Flow Rate 2 = 0.082 m/s.

T [°C]	a	b	с	a	b	с	a	b	с
		5.000			7.500			10.000	
5	-1,6E+05	1,4E+05	-3,1E+04	-2,4E+05	2,2E+05	-5,2E+04	-3,2E+05	3,0E+05	-7,0E+04
10	-2,2E+05	$2,\!0E\!+\!05$	-4,4E+04	$-3,\!4E\!+\!05$	$3,\!1E\!+\!05$	-7,3E+04	-4,5E+05	$4{,}2\mathrm{E}{+}05$	-9,8E+04
15	-3,4E+05	3,0E+05	-6,6E+04	-5,0E+05	4,7E+05	-1,1E+05	-6,7E+05	$6,3E{+}05$	-1,5E+05
20	-5,2E+05	$4,\!6E\!+\!05$	-1,0E+05	-7,8E+05	$7,\!3E\!+\!05$	-1,7E+05	-1,0E+06	$9,\!8E\!+\!05$	-2,3E+05
25	-8,2E+05	$7,\!3E\!+\!05$	$-1,\!6E\!+\!05$	-1,2E+06	$1,\!2E\!+\!06$	-2,7E+05	$-1,\!6E\!+\!06$	1,5E+06	-3,6E+05
30	-1,3E+06	$1,\!2E\!+\!06$	-2,6E+05	-2,0E+06	$1,\!8E\!+\!06$	-4,3E+05	-2,6E+06	$2{,}5\mathrm{E}{+}06$	-5,7E+05
35	-2,1E+06	$1,\!8E\!+\!06$	-4,1E+05	-3,1E+06	$2,\!9E{+}06$	-6,8E+05	-4,2E+06	$3,\!9E{+}06$	-9,1E+05
40	-3,3E+06	$2,\!9E{+}06$	-6,5E+05	-5,0E+06	$4,\!6E\!+\!06$	-1,1E+06	-6,6E+06	$_{6,2E+06}$	-1,4E+06
45	-5,2E+06	$4,\!6E\!+\!06$	-1,0E+06	-7,8E+06	$7,\!3E\!+\!06$	-1,7E+06	-1,0E+07	$9,\!8E\!+\!06$	-2,3E+06
50	-8,2E+06	7,3E+06	-1,6E+06	-1,2E+07	$1,\!1E\!+\!07$	-2,7E+06	$-1,\!6E\!+\!07$	1,5E+07	-3,6E+06
55	-1,3E+07	1,1E+07	-2,5E+06	-1,9E+07	1,8E+07	-4,2E+06	-2,6E+07	$2,\!4E\!+\!07$	-5,6E+06
60	-2,0E+07	1,8E+07	-3,9E+06	-3,0E+07	$2,\!8E\!+\!07$	-6,5E+06	-4,0E+07	3,7E+07	-8,7E+06
65	-3,0E+07	2,7E+07	-6,0E+06	-4,5E+07	$4,2E{+}07$	-9,9E+06	-6,1E+07	5,7E+07	-1,3E+07
70	-4,6E+07	4,1E+07	-9,1E+06	-6,9E+07	$6,\!4E\!+\!07$	-1,5E+07	-9,2E+07	$^{8,6E+07}$	-2,0E+07
75	-6,9E+07	6,1E+07	-1,4E+07	-1,0E+08	9,7E+07	-2,3E+07	-1,4E+08	1,3E+08	-3,0E+07
80	-1,0E+08	$9,2E{+}07$	-2,0E+07	-1,5E+08	$1,\!4E\!+\!08$	-3,4E+07	-2,1E+08	$1,\!9E\!+\!08$	-4,5E+07
90	-2,2E+08	2,0E+08	-4,4E+07	-3,3E+08	3,1E+08	-7,3E+07	-4,5E+08	4,2E+08	-9,8E+07

Table B.7: Determination of a, b and c parameters from Equations 4.36 , 4.37 and 4.38 for 5.000, 7.500 and 10.000 [ppm] of $[\text{HCO}_3^-]$ initial concentration solution using Flow Rate 3 = 0,109 m/s.

T [°C]	a	b	с	a	b	с	a	b	с
		5.000			7.500			10.000	
5	-1,3E+05	1,1E+05	-2,5E+04	-1,9E+05	1,8E+05	-4,1E+04	-2,5E+05	2,4E+05	-5,5E+04
10	-1,8E+05	$1,\!6E\!+\!05$	-3,5E+04	$-2,\!6E\!+\!05$	$2{,}5\mathrm{E}{+}05$	-5,8E+04	-3,5E+05	$3,\!3E\!+\!05$	-7,7E+04
15	-2,6E+05	2,3E+05	-5,2E+04	-4,0E+05	3,7E+05	-8,7E+04	-5,3E+05	$5,0E{+}05$	-1,2E+05
20	-4,1E+05	$_{3,6E+05}$	-8,1E+04	-6,2E+05	5,8E+05	-1,3E+05	-8,2E+05	7,7E+05	-1,8E+05
25	-6,5E+05	5,7E+05	-1,3E+05	-9,7E+05	$9,\!1E\!+\!05$	-2,1E+05	-1,3E+06	1,2E+06	-2,8E+05
30	-1,0E+06	9,1E+05	-2,0E+05	-1,5E+06	$1,\!4E\!+\!06$	-3,4E+05	-2,1E+06	1,9E+06	-4,5E+05
35	$-1,\!6E\!+\!06$	1,5E+06	-3,2E+05	-2,5E+06	$2,\!3E\!+\!06$	-5,4E+05	-3,3E+06	3,1E+06	-7,2E+05
40	-2,6E+06	$2,\!3E\!+\!06$	-5,1E+05	-3,9E+06	$3,\!6E\!+\!06$	-8,5E+05	-5,2E+06	$4,\!9E{+}06$	-1,1E+06
45	-4,1E+06	$3,\!6E\!+\!06$	-8,1E+05	-6,2E+06	$5{,}8\mathrm{E}{+}06$	-1,3E+06	-8,2E+06	7,7E+06	-1,8E+06
50	-6,4E+06	5,7E+06	-1,3E+06	-9,7E+06	$9,\!1E\!+\!06$	-2,1E+06	-1,3E+07	$1,\!2E\!+\!07$	-2,8E+06
55	-1,0E+07	8,9E+06	-2,0E+06	-1,5E+07	$1,\!4E\!+\!07$	-3,3E+06	-2,0E+07	1,9E+07	-4,4E+06
60	$-1,\!6E\!+\!07$	$1,\!4E\!+\!07$	-3,1E+06	-2,3E+07	$2{,}2\mathrm{E}{+}07$	-5,1E+06	-3,1E+07	$2,\!9E{+}07$	-6,8E+06
65	-2,4E+07	2,1E+07	-4,7E+06	$-3,\!6E\!+\!07$	$3,\!3E\!+\!07$	-7,8E+06	-4,8E+07	4,5E+07	-1,0E+07
70	$-3,\!6E\!+\!07$	$3,\!2E\!+\!07$	-7,1E+06	$-5,\!4E\!+\!07$	5,1E+07	-1,2E+07	-7,3E+07	$6,8E{+}07$	-1,6E+07
75	-5,4E+07	$4,\!8E\!+\!07$	-1,1E+07	-8,2E+07	$7,\!6E\!+\!07$	-1,8E+07	-1,1E+08	1,0E+08	-2,4E+07
80	-8,1E+07	7,2E+07	-1,6E+07	-1,2E+08	1,1E+08	-2,7E+07	$-1,\!6E\!+\!08$	1,5E+08	-3,6E+07
90	-1,8E+08	$1,\!6E\!+\!08$	-3,5E+07	-2,6E+08	2,5E+08	-5,7E+07	-3,5E+08	3,3E+08	-7,7E+07

B.1.4 Determination of mass deposition rate from Equations 4.35 and 4.32.

Table B.8: Determination of mass deposition rate $\text{Kg/m} \cdot \text{s}^2$ from Quan *et al.* [6] method for 5.000, 7.500 and 10.000 [ppm] of [HCO₃⁻] initial concentration solution.

T [°C]	5.000	7.500	10.000	5.000	7.500	10.000	5.000	7.500	10.000
	Flow	Rate 1 [[m/s]	Flow	Rate 2	[m/s]	Flow	Rate 3 [m/s]
5	2,2E-05	3,4E-05	4,6E-05	3,1E-05	4,8E-05	6,5E-05	3,9E-05	6,1E-05	8,2E-05
10	$3,\!1\text{E-}05$	$4,\!9\text{E-}05$	$6,\!6E-\!05$	$4,\!3E-\!05$	$6,\!9E-05$	$9,\!2E-05$	5,5E-05	8,7E-05	1,2E-04
15	$4,\!0\text{E-}05$	$6,\!4\text{E-}05$	8,6E-05	5,7E-05	8,9E-05	1,2E-04	$7,\!2E-05$	1,1E-04	1,5E-04
20	$5,\!0 ext{E-}05$	$7,\!9E-05$	1,1E-04	7,0E-05	1,1E-04	1,5E-04	$8,\!9E-05$	$1,\!4\text{E-}04$	1,9E-04
25	$6,\!0 ext{E-}05$	9,5E-05	1,3E-04	$8,\!4\text{E-}05$	$1,\!3E-04$	1,8E-04	$1,\!1\text{E-}04$	1,7E-04	2,3E-04
30	$7,\!0E-05$	1,1E-04	1,5E-04	$9,\!8\text{E-}05$	1,5E-04	2,1E-04	$1,\!2E-04$	$2,\!0\text{E-}04$	2,6E-04
35	$^{8,0E-05}$	$1,\!3E-04$	1,7E-04	1,1E-04	$1,\!8E-04$	$2,\!4\text{E-}04$	$1,\!4\text{E-}04$	2,2E-04	3,0E-04
40	$9,\!0E-\!05$	$1,\!4\text{E-}04$	$1,\!9E-04$	$1,\!3E-04$	$2,\!0\text{E-}04$	2,7E-04	$1,\!6E-04$	2,5E-04	3,4E-04
45	$1,\!0E-04$	$1,\!6E-04$	2,1E-04	$1,\!4\text{E-}04$	2,2E-04	$2,\!9\text{E-}04$	$1,\!8E-04$	$2,\!8\text{E-}04$	3,7E-04
50	$1,\!1E-04$	1,7E-04	$2,\!3\text{E-}04$	1,5E-04	$2,\!4\text{E-}04$	$3,\!2E-04$	$1,\!9E-04$	3,1E-04	4,1E-04
55	$1,\!2E-04$	$1,\!9E-04$	2,5E-04	1,7E-04	$2,\!6\text{E-}04$	$3,\!5E-04$	2,1E-04	$3,\!4\text{E-}04$	4,5E-04
60	$1,\!3E-\!04$	$2{,}0\text{E-}04$	$2{,}7\text{E-}04$	$1,\!8E-04$	$2{,}9\text{E-}04$	$3,\!8E-04$	2,3E-04	$3,\!6E-04$	4,9E-04
65	$1,\!4\text{E-}04$	2,2E-04	$3,\!0E-04$	$2,\!0\text{E-}04$	3,1E-04	4,1E-04	2,5E-04	$3,\!9E-04$	5,3E-04
70	1,5E-04	$2,\!4\text{E-}04$	$3,\!2E-04$	2,1E-04	$3,\!3E-04$	$4,\!4\text{E-}04$	2,7E-04	4,2E-04	5,6E-04
75	$1,\!6E-04$	2,5E-04	$3,\!4\text{E-}04$	$2,\!2\text{E-}04$	$3,\!5E-04$	4,7E-04	$2,\!8\text{E-}04$	4,5E-04	6,0E-04
80	1,7E-04	2,7E-04	$3,\!6E-04$	$2,\!4\text{E-}04$	3,8E-04	$5,\!0 ext{E-}04$	$3,\!0\text{E-}04$	4,8E-04	6,4E-04
90	$1,\!9E-04$	$3,\!0E-04$	$4,\!0\text{E-}04$	2,7E-04	4,2E-04	$5,\!6E-04$	$3,\!4\text{E-}04$	$5,\!3E-04$	7,1E-04

						-			
T [°C]	5.000	7.500	10.000	5.000	7.500	10.000	5.000	7.500	10.000
	Flow	Rate 1	[m/s]	Flow	Rate 2	[m/s]	Flow	Rate 3 [m/s]
5	4,4E-05	6,9E-05	9,3E-05	6,1E-05	9,7E-05	1,3E-04	7,8E-05	1,2E-04	1,6E-04
10	$6,\!2E-\!05$	9,8E-05	1,3E-04	8,7E-05	$1,\!4\text{E-}04$	1,8E-04	1,1E-04	1,7E-04	2,3E-04
15	8,1E-05	1,3E-04	1,7E-04	1,1E-04	1,8E-04	2,4E-04	$1,\!4\text{E-}04$	2,3E-04	3,0E-04
20	1,0E-04	1,6E-04	2,1E-04	1,4E-04	2,2E-04	3,0E-04	1,8E-04	2,8E-04	3,8E-04
25	1,2E-04	$1,\!9E-04$	2,5E-04	1,7E-04	2,7E-04	3,6E-04	2,1E-04	$3,\!4\text{E-}04$	4,5E-04
30	1,4E-04	2,2E-04	3,0E-04	2,0E-04	3,1E-04	4,1E-04	2,5E-04	3,9E-04	5,2E-04
35	1,6E-04	2,5E-04	3,4E-04	2,2E-04	3,5E-04	4,7E-04	2,8E-04	4,5E-04	6,0E-04
40	1,8E-04	2,8E-04	3,8E-04	2,5E-04	4,0E-04	5,3E-04	3,2E-04	$5,\!0 ext{E-}04$	6,7E-04
45	2,0E-04	3,2E-04	4,2E-04	2,8E-04	4,4E-04	5,9E-04	3,5E-04	5,6E-04	7,5E-04
50	2,2E-04	3,5E-04	4,6E-04	3,1E-04	4,9E-04	6,5E-04	3,9E-04	6,2E-04	8,2E-04
55	2,4E-04	3,8E-04	5,1E-04	3,4E-04	5,3E-04	7,1E-04	4,3E-04	6,7E-04	9,0E-04
60	2,6E-04	4,1E-04	5,5E-04	3,6E-04	5,7E-04	7,7E-04	4,6E-04	7,3E-04	9,8E-04
65	2,8E-04	4,4E-04	5,9E-04	3,9E-04	6,2E-04	8,3E-04	5,0E-04	7,8E-04	1,1E-03
70	3,0E-04	4,7E-04	6,3E-04	4,2E-04	6,6E-04	8,9E-04	5,3E-04	8,4E-04	1,1E-03
75	3,2E-04	5,0E-04	6,8E-04	4,5E-04	7,1E-04	9,5E-04	5,7E-04	9,0E-04	1,2E-03
80	3,4E-04	5,4E-04	7,2E-04	4,8E-04	7,5E-04	1,0E-03	6,0E-04	9,5E-04	1,3E-03
90	3,8E-04	6,0E-04	8,0E-04	5,3E-04	8,4E-04	1,1E-03	6,7E-04	1,1E-03	1,4E-03

Table B.9: Determination of mass deposition rate Kg/m \cdot s² from Andritsos *et al* [7] method for 5.000, 7.500 and 10.000 [ppm] of [HCO₃⁻] initial concentration solution.

Appendix C

Tube Blocking Test

C.1 TBT Geometry Influence

Table C.1: Statistical Analysis of Influence of Geometry over the Deposition Time using TBT System for 3.000, 4.000, 5.000, 7.500 and 10.000 [ppm] of $[\text{HCO}_3^{-}]$ initial concentration solution.

	3.000	4.000	5.000	7.500	10.000	3.000	4.000	5.000	7.500	10.000
Diameter [in]			1/8					1/16		
Ν	5	4	6	6	6	3	3	3	3	6
Degrees of Freedom	4	3	5	5	5	2	2	2	2	5
Mean [s]	1055	800	748	610	562	427	377	335	318	324
Standar Deviation	142	86	90	83	67	30	17	5	17	43
Alpha	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$
Confidence Interval	125	84	72	66	53	34	19	6	19	35
Error	12	10	10	11	9	8	5	2	6	11
Top C.I.	1180	884	819	676	615	460	396	340	337	359
Bottom C.I.	931	716	676	543	509	393	358	329	298	290

C.2 TBT Flow Rate Influence

Table C.2: Statistical Analysis of Influence of Flow Rate over the Deposition Time using TBT System for 5.000, 7.500 and 10.000 [ppm] of $[HCO_3^{-}]$ initial concentration solution.

	5.000	7.500	10.000	5.000	7.500	10.000	5.000	7.500	10.000
	Flow	Rate 1	[m/s]	Flow	Rate 2	2 [m/s]	Flow	Rate 3	[m/s]
N	6	7	6	7	7	6	6	6	6
Degrees of Freedom	5	6	5	6	6	5	5	5	5
Mean [s]	1355	997	884	905	664	636	748	610	562
Standar Deviation	76	68	103	136	46	12	90	83	67
Alpha	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$
Confidence Interval	61	50	83	101	34	10	72	66	53
Error	4	5	9	11	5	2	10	11	9
Top C.I.	1416	1047	967	1006	699	646	819	676	615
Bottom C.I.	1294	946	801	805	630	626	676	543	509

C.3 TBT With Experimental Mass Gain

Table C.3: Experimental Mass Gain [g] using TBT System for 5.000, 7.500 and 10.000 [ppm] of $[HCO_3^{-}]$ initial concentration solution.

5.000	7.500	10.000	5.000	7.500	10.000	5.000	7.500	10.000
Flow	Rate	1 [m/s]	Flow	Rate 2	2 [m/s]	Flow	Rate 3	[m/s]
0,176	0,193	0,488	0,193	0,489	0,516	0,078	0,276	0,692
$0,\!148$	$0,\!360$	$0,\!595$	$0,\!162$	$0,\!223$	$0,\!471$	$0,\!175$	$0,\!219$	0,610
$0,\!228$	$0,\!139$	0,212	0,077	$0,\!196$	$0,\!580$	0,206	$0,\!187$	$0,\!525$

	5.000	7.500	10.000	5.000	7.500	10.000	7.500	10.000	5.000
		F1			F2			F3	
N	3	3	3	3	3	3	3	3	3
Degrees of Freedom	2	2	2	2	2	2	2	2	2
Mean [g]	0,184	$0,\!231$	0,432	$0,\!144$	0,303	0,522	0,228	0,609	$0,\!153$
Standar Deviation	0,040	$0,\!116$	$0,\!197$	0,060	0,162	$0,\!055$	$0,\!045$	0,083	0,067
Alpha	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$	$0,\!95$
Confidence Interval	0,045	$0,\!131$	0,223	0,068	$0,\!184$	0,062	$0,\!051$	0,094	0,076
Error	24,7	56,7	51,7	$47,\!4$	60,7	11,8	$22,\!5$	$15,\!5$	$49,\!6$
Top C.I.	0,229	$0,\!361$	$0,\!655$	0,212	$0,\!486$	$0,\!584$	$0,\!279$	0,703	0,229
Bottom C.I.	0,138	0,100	0,208	0,076	0,119	$0,\!461$	$0,\!176$	0,515	0,077

Table C.4: Statistical Analysis of Experimental Mass Gain using TBT System for 5.000, 7.500 and 10.000 [ppm] of $[\text{HCO}_3^-]$ initial concentration solution.

Appendix D LTS Loop Design

Table D.1: Prediction of Calcium Carbonate Mass Deposition [Kg] on Time using Quan's and Andritsos' Models for 5.000, 7.500 and 10.000 [ppm] of $[\text{HCO}_3^{-}]$ initial concentration solution.

Time [s]	5.000	7.500	10.000	5.000	7.500	10.000
		Quan		1	Andritsos	5
1	3,9E-07	6,1E-07	8,2E-07	7,7E-07	1,2E-06	1,6E-06
60	$2{,}3\text{E-}05$	3,7E-05	$4{,}9\text{E-}05$	$4{,}6\text{E-}05$	$7,\!3E-05$	9,8E-05
3.600	$1,\!4\text{E-}03$	$2{,}2\text{E-}03$	$2{,}9\text{E-}03$	$2,\!8\text{E-}03$	$4{,}4\text{E-}03$	5,9E-03
7.200	$2{,}8\text{E-}03$	$4{,}4\text{E-}03$	$5,\!9\text{E-}03$	$5,\!6E-03$	$8{,}8\text{E-}03$	1,2E-02
14.400	$5,\!6E-03$	$8{,}8\text{E-}03$	1,2E-02	1,1E-02	$1,\!8\text{E-}02$	$2,\!4\text{E-}02$
28.800	1,1E-02	$1,\!8\text{E-}02$	$2{,}4\text{E-}02$	$2{,}2\text{E-}02$	3,5E-02	4,7E-02
57.600	$2{,}2\text{E-}02$	3,5E-02	$4{,}7\text{E-}02$	$4{,}5\text{E-}02$	$7,\!0E-02$	9,4E-02
86.400	3,3E-02	5,3E-02	7,1E-02	$6{,}7\text{E-}02$	$1,\!1E-01$	1,4E-01