PREDICTING STRONTIUM CARBONATE PRECIPITATION THROUGH REGRESSION

A FOCUS ON RECOVERY FROM REVERSE OSMOSIS CONCENTRATE

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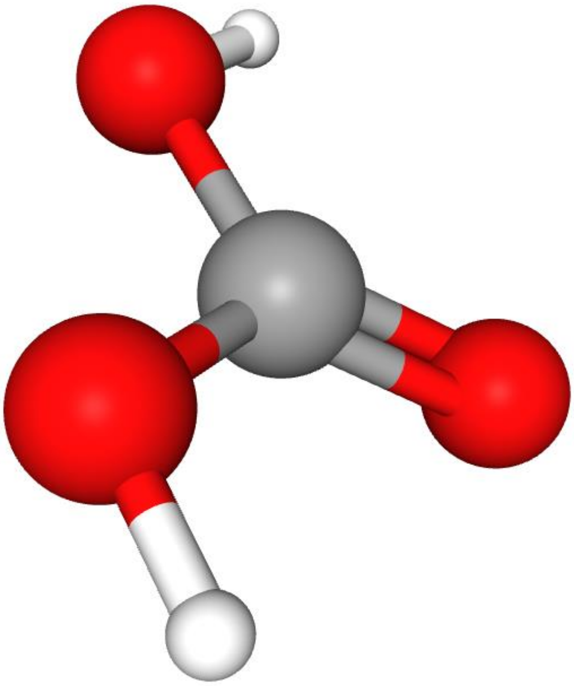

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Predicting strontium carbonate precipitation through regression

A focus on recovery from reverse osmosis concentrate

By

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Preface

This report presents the culmination of all work carried out for a Master's thesis specializing in Environmental Engineering at TU Delft. This thesis topic evolved from what was originally an internship offer from Witteveen+Bos. The original internship offer was based on one of their internal projects, Saline Water Opportunity. While the aim of this thesis is substantially different from what the internship was for, the goals of the internship have been addressed and integrated into this thesis. A total of eight months was invested in performing this research. This project was in coordination with Witteveen+Bos who provided me access to not only OLI Studio software but also consistent support in the form of guidance and sharing their personal experience and knowledge amongst other things.

This report is aimed at any individual who is interested in the fields of either precipitation of strontium, resource recovery, design of experiments application or a combination of the above. At the time of working on this report there was an observable gap in literature in the described areas. A personal affinity for exploring resource recovery coupled with the knowledge of how useful the concept of design of experiment could be, prompted me to address the knowledge gaps about strontium and resulted in this trinity of topics. This report could also act as a guide to anyone seeking to address similar challenges.

Acknowledgements

I would like to offer my deepest gratitude to Dr. Ir. Henri Spanjers, the chair of my thesis committee for not only guiding me throughout this challenging period but also motivating me to define my own research topic. I would also like to extend my sincerest gratitude to the rest of my thesis committee, Prof. Dr. Ir. Jan Peter van der Hoek, Dr. Boris van Breukelen and Dr. Sirous Ebrahimi for their guidance, valuable feedback and also the accommodations they allowed to help me complete my thesis in these challenging times of a pandemic.

From Witteveen+Bos, I would like to thank Mr. Sytze Terwisscha van Scheltinga for allowing me an opportunity to define my own research goals through their internship and his guidance. Lastly, I would like to specially thank Ir. Eleftheria Chiou who has been like an anchor throughout the duration my thesis be it providing technical guidance, answering the silliest of questions or even taking time outside working hours to help me out when it was not warranted. It would not have been possible for me to complete my thesis without the support of others.

Delft, November 2020
Asiman Dash

Summary

Keywords: Precipitation, Strontium Carbonate, Reverse Osmosis Concentrate, Box–Behnken Design, Recovery, OLI Studio

Resource recovery from waste streams is indispensable to the shift from a linear economy to a circular economy. Industrial concentrate is a waste stream that is being actively researched to explore and expand the prospects of resource recovery. Strontium (Sr), an alkaline earth metal, while found quite regularly in concentrate streams has not been a focus for recovery. Through this study, the recovery of Sr as strontium carbonate ($SrCO_3$) via precipitation from concentrate streams has been investigated. The objective of this study is to characterize $SrCO_3$ precipitation in terms of factors that influence it. Specifically, the effect of multiple factors has been investigated on the amount of Sr precipitated (as % relative to the initial amount of Sr) as well as the purity of the corresponding $SrCO_3$ precipitate (%).

Factors that could affect either the amount of Sr precipitated or the purity of the precipitated $SrCO_3$ were identified based on theoretical knowledge. Equilibrium-based simulations were performed using OLI studio to confirm their impact. The conditions associated with the identified influencing factors were investigated in concentrate produced from a reverse osmosis unit during drinking water production at Puur Water & Natuur (PWN). A Box-Behnken Design was implemented to quantify the relationship between the identified factors and two responses (i) Amount of Sr precipitated and, (ii) Purity of $SrCO_3$ precipitated. The range of the factors in the design was established based on their ranges as observed in the PWN concentrate.

The value of pH and concentrations of strontium, inorganic carbon (C), calcium (Ca), barium (Ba) and inorganic sulfur (S) were hypothesized to have quantitative and qualitative effects on the $SrCO_3$ precipitated in an aqueous solution. Magnesium (Mg) was hypothesized to have only a qualitative effect on the $SrCO_3$ precipitated. Direct $SrCO_3$ precipitation from PWN concentrate was not practical due to the considerably higher concentration of other ions. To facilitate $SrCO_3$ precipitation from PWN concentrate, the concentration of the other ions was reduced in the concentrate by recovering them in the form of precipitates. The recovery of these precipitates was investigated through variation of pH, temperature and pressure via OLI simulations. Theoretically, it is possible to recover 0.0014 g of $SrCO_3$ (100% purity) per liter of concentrate along with 0.684 g $CaCO_3$ (99.95% purity), 0.161 g $Mg(OH)_2$ (96% purity), 0.0083 g $Ca(OH)_2$ (99.99% purity) and a NaCl solution (4.65 M). Using the Box-Behnken Design, the mathematical relationship between the amount of Sr precipitated (as % relative to initial concentration) and purity of $SrCO_3$ precipitated (%) subject to the identified factors was established. The equations had a R^2 of 98.75% and 97.38% respectively. S was found to not have any significant impact on $SrCO_3$ precipitation while a positive interaction effect between Sr and Ca was also identified.

$$
\begin{aligned}
\%\mathrm{Sr\ precipitated} &= 0.82098 + 0.01319\,\mathrm{pH} - 0.04004\,\mathrm{Sr} + 0.11581\,\mathrm{C} - 0.07343\,\mathrm{Ca} - 0.01314\,\mathrm{pH} \\
&\quad * \mathrm{pH} - 0.04299\,\mathrm{Sr} * \mathrm{Sr} - 0.04073\,\mathrm{C} * \mathrm{C} - 0.02041\,\mathrm{Mg} * \mathrm{Mg} + 0.01818\,\mathrm{pH} * \mathrm{Ca} \\
&\quad + 0.05369\,\mathrm{Sr} * \mathrm{C} + 0.07436\,\mathrm{Sr} * \mathrm{Ca} - 0.05763\,\mathrm{C} * \mathrm{Ca}
\end{aligned}
$$

$$
\begin{aligned}
\mathrm{SrCO_3\ purity\ (\%)} &= 0.5155 - 0.20923\,\mathrm{pH} + 0.12593\,\mathrm{Sr} - 0.03178\,\mathrm{C} - 0.06115\,\mathrm{Ca} - 0.07187\,\mathrm{Mg} \\
&\quad + 0.0617\,\mathrm{pH} * \mathrm{pH} - 0.0388\,\mathrm{Sr} * \mathrm{Sr} - 0.0295\,\mathrm{C} * \mathrm{C} + 0.0456\,\mathrm{Mg} * \mathrm{Mg} - 0.0485\,\mathrm{pH} \\
&\quad * \mathrm{Sr} + 0.0595\,\mathrm{pH} * \mathrm{C} + 0.0405\,\mathrm{pH} * \mathrm{Ca} - 0.0903\,\mathrm{pH} * \mathrm{Mg} + 0.0481\,\mathrm{Sr} * \mathrm{C} \\
&\quad + 0.0614\,\mathrm{Sr} * \mathrm{Ca} - 0.0453\,\mathrm{C} * \mathrm{Ca}
\end{aligned}
$$

The predictive R^2 associated with these equations are 93.45% and 86.32% respectively. This is representative of the accuracy of the developed equation in prediction and hence their applicability to replace experiments and simulations to for quick yet reliable results. These equations, however, are built on the outputs of OLI simulations. Therefore, their accuracy is subject to the predictive capability of OLI software. Experimental results based on the chosen Box-Behnken Design are needed to either replace the OLI simulations results entirely or account for the inaccuracy of OLI simulations.

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List of Abbreviations

Ω	Saturation State	**Mg**	Magnesium
°C	degree Celsius	**$Mg(OH)_2$**	Magnesium Hydroxide
atm	Atmospheric pressure	**mg**	Milligram
Ba	Barium	**mL**	Millilitre
$BaSO_4$	Barium Sulphate	**mM**	Millimolar
BBD	Box Behnken Design	**M**	Molar
Ca	Calcium	**NF**	Nanofiltration
$CaCO_3$	Calcium Carbonate	**NOM**	Natural Organic Matter
$Ca(OH)_2$	Calcium Hydroxide	**N.A**	Not Applicable
C	Inorganic Carbon	**N.D.**	Not Detected
CO_2	Carbon Dioxide	**Na**	Sodium
CO_3^{2-}	Carbonate ion	**NaOH**	Sodium Hydroxide
CCD	Central Composite Design	**OH^-**	Hydroxide ions
Cl	Chloride	**P**	Pressure
Coef	Coefficient	**PWN**	Puur, Water & Natuur
DoE	Design of Experiments	**R^2**	Coefficient of Determination
g	Gram	**RO**	Reverse Osmosis
HCO_3^-	Bicarbonate ion	**SI**	Saturation Index
IAP	Ion Activity Product	**SWRO**	Sea water reverse osmosis
ICP-MS	Inductively coupled plasma mass spectrometry	**Sr**	Strontium
iP	Inorganic Phosphorus	**$SrCO_3$**	Strontium Carbonate
IS	Ionic Strength	**$SrSO_4$**	Strontium Sulphate
K_{sp}	Solubility Product	**S**	Inorganic Sulphur
L	Litre	**T**	Temperature

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1. Introduction

Chapter Summary: **In this chapter, the motivation behind this thesis is established. The potential of recovering strontium from concentrate streams is explored. Arguments for choosing precipitation as the method of recovery along with the choice to recover strontium as strontium carbonate are provided. Lastly, the research objectives and questions are defined, and the approach undertaken to address the research questions is presented as well.**

1.1. Resource recovery and concentrate

Climate change represents a global issue directly linked to human activities[1][2]. To tackle the climate change crisis, various adaption[3] and mitigation strategies[4] have been considered. Transition to a circular economy from the current linear economy represents one such mitigation strategy[5] that has received global attention[6][7][8][9]. An indispensable component to the establishment and development of a successful circular economy is the recovery of resources from various industrial streams.

Resource recovery can be understood as the recovery of useful materials/resources from waste streams aimed at either re-using them as secondary resources in different processes or recycling them within the same process. By doing so both, the requirement for primary resources and the amount of waste generated, are reduced. The concept of resource recovery can be adapted to various industrial sectors[10][11][12][13]. Based on the composition of the waste stream, the resources recovered vary from energy[14][15] to nutrients[16] to various chemicals[17][18].

Practising resource recovery from liquid waste streams is being increasingly explored as an industry practice. Water is a primary necessity for almost all industries for various purposes including reaction medium, cooling, process ingredient, steam generation, cooling, cleaning, transport etc.[19]. And in almost all cases where water is used, a liquid waste stream is produced. In 2018 alone, more than 3 billion m^3 of water was used for manufacturing in the Netherlands[20]. Depending on the local regulations, this liquid waste stream is treated to different degrees and discharged into various water bodies. And, in cases where the waste stream is not treated adequately, their discharge leads to issues such as eutrophication[21], increased salinity[22], toxicity[23], long term temperature fluctuation[24] etc. The quality of these waste streams varies depending on the process from which they are produced but, in many cases, contain a valuable component/s which could find applications in other processes.

If these valuable components can be recovered in a reusable form (directly or through further upcycling), it would reduce the overall production demand for the component. Continuous and consistent recovery of the component would imply a transition to a circular economy where the total amount of that particular resource is a cycle is conserved. Hence, there would be no/reduced need for further production of that resource. The indirect implication of the recovery would be reducing/minimizing the environmental impacts and costs of mining, transportation, energy and chemical consumption associated with the primary production of the resource. Therefore, practicing resource recovery on such a waste stream acts as a mitigating strategy for climate change and also reduces the total amount of pollution.

A common liquid waste stream produced in industries is concentrate, a concentrated solution of mixed and directly unusable components. What could be undesirable for one process could be necessary, useful and valuable for a different process. The formation of concentrates is inevitable when filtration/membrane-based techniques are employed. The composition of the concentrate is subject to the feed quality, process conditions and product quality. The drinking water industry often employs filtration techniques such as ultrafiltration (UF) and reverse osmosis (RO) to meet the high-quality requirements of drinking water. A concentrate stream represents a good prospect to practice resource recovery on due to its concentrated nature and cost associated with its disposal. Within the water industry, the concept of resource recovery is being actively applied and even explored further[25][26][27][28]. Some of the resources being explored for potential recovery include water[29], energy[30], and various chemicals[31].

1.2. Focussing on Strontium

The resource targeted for recovery is this study is Strontium. Strontium (Sr) is an alkaline earth metal found naturally in the minerals of celestine ($SrSO_4$) and strontianite ($SrCO_3$). Sr can be commonly found in nature with an estimated crustal abundance of 370 mg/kg and oceanic abundance of 7.9 mg/L[32]. The physical characteristics and chemical nature of Sr are generally in-between that of calcium (Ca) and barium (Ba)[33], its group neighbours. Some of the properties of Sr can be seen below in Table 1.

Table 1: Properties of strontium (Sr)

Property	**Value**[32]
Atomic Number	38
Atomic Weight	87.62
Melting Point	777 °C
Boiling Point	1382 °C
Density	2640 kg/m^3
Oxidation State	+2

Given its abundance, Sr is found in almost every natural water body and hence can also be usually found in concentrate streams from drinking water production which source their feed from natural water bodies. However, owing to it relatively lower concentration the recovery of Sr has not been looked into extensively. A literature review from 2014 stated that at that point in time, large scale strontium extraction from desalination concentrate did not exist and remained doubtful in the immediate future[25]. While research has been carried out to look into the possibility of removal and/or recovery of Sr from sea water directly[34][35][36] or from radioactive waste streams [37][38][39][40], only one study was found which had an indirect focus on the recovery of Sr from concentrate[41]. While the relatively lower concentrations of Sr primarily present an economic barrier to its recovery, the technical feasibility for its recovery should be established, nonetheless. Table 2 shows the various Sr concentrations measured in different aqueous streams. It can be observed that Sr concentration in the concentrate varies depending on its source. Sr finds commercial applications in a variety of way, as can be seen in Table 3. Therefore, theoretically there is an economical argument to consider Sr recovery.

It has been observed that under specific conditions, the presence of Sr can promote faster growth of calcium carbonate ($CaCO_3$) [42], a known scalant. Presence of Sr can also lead to scaling in the form of strontium sulphate ($SrSO_4$)[43]. If the same water body is used as a feed source and discharge point it would lead to higher localised Sr concentrations. This could further lead to problems such as increased scaling if the water is used for oilfield operations, steam generation, cooling or passed through a membrane. Therefore, depending on its initial concentration, the recovery of Sr could lead to a proportional decrease in salinity of concentrate (and hence of the discharge body) and also act as a passive measure against scaling for future operations.

Table 2: Sr concentration in different aqueous streams

	Concentration (mg/L)	**Reference**
Fresh Water		
Surface freshwater	0.08	[44]
Rhine river - Netherlands		
Lobith	0.316 – 0.545	[45]
Nieuwegin	0.334 – 0.466	
Niewuwersluis	0.359 – 0.482	
Andijk	0.397 – 0.503	
Saline Water		
North Atlantic Sea	7.2 – 7.8	[46]
Surface Seawater	8.13	[47]
Waste Streams		
SWRO[1]		
Assadanat	28.2	[48]
Abu - Mudhaibi	26.9	
Haima	23.9	
WWRO[2]		
Facility 1	4.73	[49]
Facility 2	4.23	
Landfill Leachate		
A	2.37	[50]
B	3.83	[51]
Zero Brine		
Feed	35.3	[52]
Evaporator Effluent	139.6	

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[1] Sea water reverse osmosis concentrate

[2] Wastewater reverse osmosis concentrate

Table 3: Applications of different forms of Sr

Form	**Applications**[53]
Strontium compounds	
Strontium bromide	Optic materials, components of special glass and luminophores.
Strontium carbonate	Ceramic ferrite magnets, ceramic glazes, anticorrosion and fluorescent paints, hi-tech ceramics, pyrotechnics. Semi – product for synthesis of other strontium compounds.
Strontium chloride	Pyrotechnic compositions, components of special glass and luminophores.
Strontium chromate	Yellow pigment in the production of lacquers and paints, primer component for light metals and alloys in aircraft building.
Strontium fluoride	Optic materials, components of special glass and luminophores
Sodium hexaferrite	Magnetic material
Strontium iodide	Scintillation counters, components of special glass and luminophores
Strontium nitrate	Component for pyrotechnic compounds
Strontium oxide	Component of oxide cathodes of electron emitters in electro-vacuum devices, high temperature superconductors and pyrotechnical mixtures; Raw material to produce strontium metal; Mat glaze
Strontium sulphate	Filling material in production of paints and rubber
Strontium sulphide	Component of luminophores and fluorescent compounds
Strontium titanate	Ferroelectric material, component of piezo – ceramics; material for dielectric antenna and phase shifters; production of nonlinear capacitors and infrared sensors; Main form of ^{90}Sr in radioactive sources and radioisotope thermoelectric generators
Stable isotopes	Rubidium – Strontium Dating
	Geographic tracing
Radioactive Isotopes	
^{82}Sr	Formation of ^{82}Rb
^{85}Sr	Radiotracer in radiochemical studies; Imaging in nuclear medicine
^{89}Sr	Nuclear medicine for palliative therapy of bone tumours.
^{90}Sr	Beta emitter in beta sources and energy sources, Parent nuclide for 90Y generators in nuclear medicine, Calibration sources for radiometers and dosimeters

1.3. Recovering strontium via precipitation

To recover resources effectively, the targeted component must be separated from the unrequired components to the largest extent possible. The separation can be based on physical and/or chemical properties of the components. Physical properties such as size allow for separation of components using membrane based technologies such as ultrafiltration or reverse osmosis. Chemical properties such as charge and bond energy can be used to separate components via techniques such as ion exchange, electrolysis etc.

Precipitation, a technique based on chemical properties, is defined as “Sedimentation of a solid material (precipitate) from a liquid solution in which the material is present in amounts greater than its solubility in the liquid” [54]. If only specific components can be (over)saturated under specific conditions, then precipitation can be applied to separate the target component from the unwanted components in a mixed solution. Thus, precipitation can be used as a purification or concentration step for the application of resource recovery. Precipitation already finds use in treatment schemes of various liquid waste streams[55][56][57].

While the term “Crystallization” is commonly used interchangeably with precipitation, they differ in their mechanism. The formation of a solid phase in precipitation is on account of the insolubility of the precipitate while in crystallisation, a crystal solid is formed specifically due to lowering the temperature or evaporating the solvent[58]. In this report, the terms of crystallisation and precipitation are not used in an exchangeable manner.

The choice of technology and/or method for recovery purposes is dependent on a number of factors such as the nature of the target component and the matrix of other components it is mixed with. Realistically, a number of technologies such as nanofiltration (NF), ion exchange, adsorption etc. can be applied to recovery Sr specifically. However, the application of precipitation has general practical advantages over other alternatives. Compared to membrane based separation techniques, precipitation does not require anti-scalants, mandatory high operating pressures and backwashing. Compared to ion exchange, there is no need for the development of expensive resins/modules and their regular regenerations. Electrodialysis, while obtaining the required separation of Sr, presented the issue of high power consumption[59]. Precipitation can be specific in behaviour and can be brought about by simple changes in process conditions such as pH.

While applying precipitation certainly has its practical advantages, it also has its drawbacks. The common drawbacks on applying precipitation include substantial chemicals consumption, high sensitivity to changes in chemical composition of feed and presence of anti-scalants in waste streams such as concentrate.

Physiochemical adsorption and ion exchange methods for the removal of Sr have been explored extensively [53]. The relatively lower amount of literature for recovering Sr via precipitation makes it an attractive proposition in terms of research. Moreover, with development of software such as PHREEQC[60] and OLI[61], it becomes possible to simulate precipitation in an increasingly detailed and advanced fashion. Therefore, due to the simplicity yet usefulness of precipitation, it was considered as the technique to recovery Sr.

1.4. Precipitating strontium as strontium carbonate

Based on the behaviour of different strontium compounds, it is theoretically possible to precipitate Sr in more than one form. However, for this study the focus was on precipitating Sr in the form of strontium carbonate ($SrCO_3$). The choice of $SrCO_3$ was based on three separate arguments:

- *<u>Practical Basis</u>*: $SrCO_3$ has a low solubility. The solubility product constant (K_{sp}) of $SrCO_3$ is 1.1 x 10^{-10} [53]. This implies that it is a realistic choice for precipitation without needing to go to extremes as opposed to Sr salts such as strontium nitrate, strontium chloride which have a high solubility. Moreover, the counter ion required to precipitated $SrCO_3$ is the carbonate ion (CO_3^{2-}). This counter ion is naturally found in substantial quantities in aqueous streams as HCO_3^- and/or dissolved CO_2. A naturally present counter ion makes it unnecessary to add it from external sources which would have been the case of precipitating Sr as strontium titanate ($SrTiO_3$). This choice of counter ion is also beneficial as it can be easily manipulated to the desired concentration through aeration/deaeration, pH adjustment etc. in comparison to counter ions such as sulphate (SO_4^{2-}).

- *<u>Economic Basis</u>*: While recovery of resources has environmental benefits, it is not feasible to practice it if the recovered resource is not valuable enough. As observed in Table 3, not only does $SrCO_3$ finds application in a number of uses, it, more importantly acts as a reagent for the production of other Sr compounds. There is an extensive demand for $SrCO_3$ in the European Economic Area (EEA) with 10,000 – 100,000 tonnes of $SrCO_3$ being manufactured and/or imported per year [62]. Therefore, recovery of $SrCO_3$ has potential for economic upsides.

- *<u>Environmental Basis</u>*: Only a few deposits of Strontianite ($SrCO_3$) have been discovered that are suitable for development. Therefore, the current production techniques involve mining of Celestine ($SrSO_4$) ores and subsequent conversion to $SrCO_3$ via processes such as a combination of roasting –

reduction or double decomposition[63]. The adverse environmental impacts of mining are well established [64] and the current production techniques are either energy or chemical intensive. Therefore, the recovery of Sr as $SrCO_3$ from a waste stream such as concentrate could significantly reduce the negative environmental impact associated with the current production techniques of $SrCO_3$.

Therefore, on account of its multiple advantages, $SrCO_3$ was considered as the precipitate form through which Sr would be recovered.

1.5. Research Objectives and Questions

The primary objective of this study is to reduce the knowledge gaps pertaining to the recovery of Sr from concentrate streams. While there is an observable lack in literature associated with recovery of Sr in general, this study specifically focuses on recovery of Sr as $SrCO_3$ via precipitation. The main research questions that seek to be answered by this study were:

1. Which factors affect the precipitation of $SrCO_3$?
2. At what values can these affecting factors be expected in industrial concentrate?
3. What is the relationship between the affecting factors and $SrCO_3$ precipitation?

The sub – questions that are answered along with the main research questions above include:

1. Can $SrCO_3$ be recovered directly from industrial concentrate?
2. Can the conditions of industrial concentrate be favourably manipulated to enhance $SrCO_3$ precipitation?
3. How much $SrCO_3$ can be recovered via precipitation from industrial concentrate?
4. How is the effect of a factor affected by the presence of another factor?
5. Is the effect of a factor statistically significant?

1.6. Report Outline

The approach undertaken for this study is represented in Figure 1. The first step in studying $SrCO_3$ precipitation is identifying the factors that influence it. For the purpose of this study a factor is defined as any quantifiable property and/or characteristic, the variation of which could influence the final equilibrium conditions associated with precipitation of $SrCO_3$. Factors considered were evaluated on a dual basis. First theoretical arguments are provided to justify whether a factor could or could not have influence on $SrCO_3$ precipitation. Following this, simulations to test the aforementioned arguments are performed using OLI Studio, an electrolyte thermodynamic framework based software which allows for equilibrium calculations. An alternate to the OLI Studio software would be using PHREEQC. However, due to certain practical and technical advantages[65] the simulations were carried out on OLI Studio over PHREEQC. Some of these advantages include a more comprehensive database and greater robustness for higher concentration systems.

Once the relevant factors were identified the next step was to analyse how these factors present themselves in real world industrial conditions. For this purpose concentrate produced at the one of the drinking water production sites of Puur, Water & Natuur (PWN)[66] was used as a case study. Simulations were once again performed using OLI studio to investigate whether the manipulation/adjustment of certain process conditions (pH, temperature and pressure) could be beneficial in improving the recovery of $SrCO_3$ in terms of either purity or the absolute amount recovered.

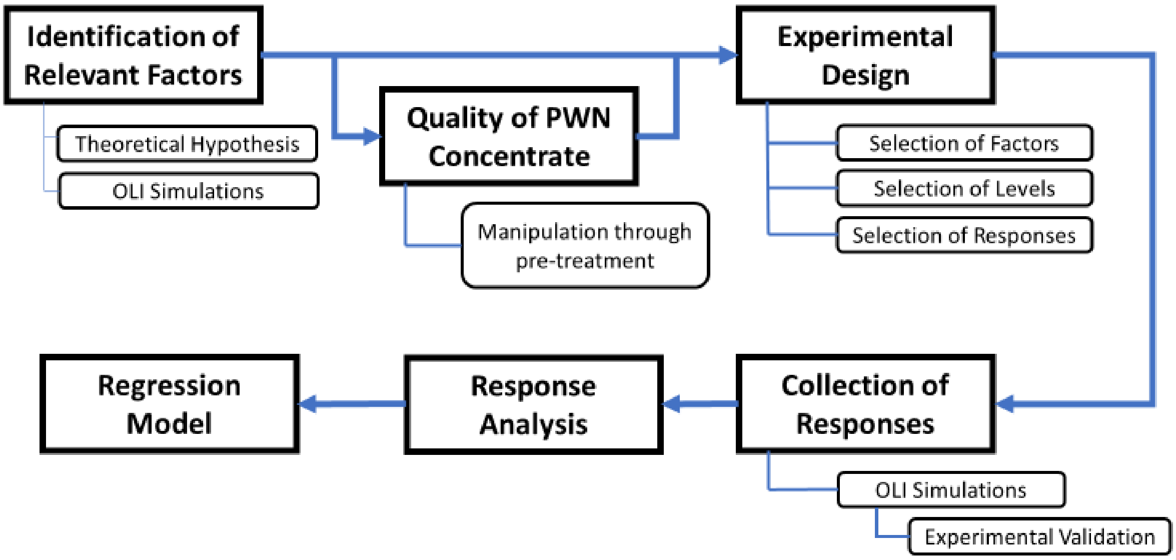

Figure 1: Overview of the approach undertaken to address the research questions and objectives of this study

The next step was to incorporate and combine the information from the previous the two steps to develop an experimental design. The main goals of this experimental design were to evaluate the differences observed in $SrCO_3$ precipitation when the relevant factors were varied while at the same time ensuring the conditions of the study are grounded in conditions that can be expected in real world. As opposed to the traditionally practiced experimental designs in which factors are varied one at a time, this study implements the concept of "Design of Experiments" (DoE). DoE has been defined as "the process of planning the experiment so that appropriate data will be collected and analysed by statistical methods, resulting in valid and objective conclusions"[67]. Through DoE, a predictive knowledge of a process can be built around its input (factors), process conditions (levels) and output (responses). A more detailed discussion of DoE is presented in the corresponding chapter (Chapter 5) and arguments are made to justify the various decisions taken to finalize the experimental design. Minitab statistical software[68] was used as a tool to develop the overall experimental design.

The following chapter deals with how the outputs (responses) for the finalized experimental design were obtained. OLI simulations represented the primary method of obtaining the desired outputs. Experiments were also undertaken to validate the performed OLI simulation. All facets related to obtaining the responses including details of the experimental set-up, the obtained output and degree of similarity between the simulated predictions and experimentally obtained outputs are discussed in this chapter (Chapter 6).

The subsequent chapters present the results from the analysis carried out on the collected outputs (responses). The analysis was carried out through Minitab statistical software. The interpretation of the results and the reasoning for observing these results are also deliberated. The overall findings from this study and the answers to the research questions being investigated are concluded in Chapter 7.

2. Identification of relevant factors

Chapter Summary: **This chapter discusses details related to identification of factors that have the potential to influence the equilibrium conditions surrounding the precipitation of $SrCO_3$. The categories under which various factors may fall into is first established. Then specific factors under each established category are explored. The categories explored include driving force, process conditions, competitors and miscellaneous factors. Arguments based on theoretical knowledge/information are made to shortlist factors that have the potential to affect $SrCO_3$ precipitation. OLI simulations are performed on these shortlisted factors to verify if any impact is actually observable or not. pH and concentrations of strontium, inorganic carbon, calcium, barium and inorganic sulphur were identified to have qualitative and quantitative effects of the precipitation outcomes of $SrCO_3$. Magnesium was observed to give only a qualitative effect on $SrCO_3$ precipitation. Temperature, pressure, ionic strength, inorganic phosphorus concentration and natural organic matter did not provide enough evidence to conclude that they have an effect on $SrCO_3$ precipitation based on final equilibrium conditions.**

2.1. Defining a Factor

A factor, for the purpose of this study, is defined as a quantifiable property and/or characteristic, the variation of which could influence the final equilibrium conditions associated with precipitation of $SrCO_3$. While there could be any number of factors that could theoretically have an impact, this study limits the factors only to those which are expected to be found naturally in aqueous solutions containing Sr. Based on the above considerations, factors have been categorized into four distinct groups.

1. Driving Force – Properties that represent the primary reason a process reaches its end state.
2. Process Conditions – Properties that define the state of a process.
3. Competitors – Properties that shift the end state of a process undesirably
4. Miscellaneous – Properties commonly associated with concentrate

While the first three categories of factors revolve around the precipitation of $SrCO_3$, the last category of miscellaneous factors was considered to identify if and how the properties of a concentrate could affect $SrCO_3$ precipitation.

2.2. Theoretical Hypothesis

With the categorization of factors finalized the next step was to select prospective factors from each category. Theoretical knowledge is used to create a shortlist of factors which could influence $SrCO_3$ precipitation. The effect of the shortlisted factors would be tested next through OLI simulations.

Driving Force

The end state of a precipitation process is based on the insolubility of the precipitating solid. The tendency of a solid to precipitate can be investigated via their saturation state or saturation index. The saturation state (Ω; Eq. (1)) and saturation index (SI; Eq. (2)) are calculated based on the Ion Activity Product (IAP; Eq.(3)) and solubility product (K_{sp}; Eq.(4)) of the component. IAP and K_{sp} in turn are calculated based on the concentrations of the individual ions that make up the precipitate.

$$\Omega_{SrCO_3} = \frac{IAP_{SrCO_3}}{K_{SrCO_3}} \qquad \text{Eq. (1)}$$

$$SI_{SrCO_3} = \log\left[\frac{IAP_{SrCO_3}}{K_{SrCO_3}}\right] \qquad \text{Eq. (2)}$$

$$IAP_{SrCO_3} = [Sr^{2+}][CO_3^{2-}] \quad \text{(at any specific time)} \qquad \text{Eq. (3)}$$

$$K_{SrCO_3} = [Sr^{2+}][CO_3^{2-}] \quad \text{(at equilibrium)} \qquad \text{Eq. (4)}$$

This essentially means that the concentration of the individual ions responsible for the formation of $SrCO_3$, i.e. Sr^{2+} and CO_3^{2-} ions are the primary driving force for the precipitation of $SrCO_3$. Hence, they are considered as factors to be studied. The precipitation reaction is presented in Eq. (5)

$$Sr^{2+} + CO_3^{2-} \rightarrow SrCO_3 \downarrow \qquad \text{Eq. (5)}$$

Considering that the anion CO_3^{2-} can exist also as bicarbonate (HCO_3^-) or dissolved carbon dioxide (CO_2) in aqueous solutions, the concentration for CO_3^{2-} was represented by the concentration of the total inorganic carbon (C). Thereby, irrespective of the species distribution, the total amount of C would always remain conserved i.e. reduce the variability associated with the potential speciation of CO_3^{2-}. The initial amount of Sr in the solution was shown to influence the degree of strontium removal in a pellet coprecipitation micro-filtration process[69]

Process Conditions

Depending on the nature of the process and the targeted end stage, a number of parameters may be used to define the state of a process. Some of the common process conditions used to characterize a process include pH, volume, temperature, pressure, conductivity, enthalpy, viscosity etc Out of the many possible parameters, the choice was limited to three potential factors.

pH : pH is a logarithmic scale used to measure the acidity or alkalinity on an aqueous solution. It is defined in terms of the activity of hydrogen ions (H^+) in a solution[70]. pH is commonly used to describe the state of a process and in many cases manipulated to reach the desired results. pH has the ability to influence the to influence the behaviour of certain components in a solution. For example, as shown in Figure 2 below, the ratio of CO_3^{2-} to HCO_3^- in an aqueous solution is dependent on the pH of the solution. As it has already been seen, the concentration of CO_3^{2-} is an important factor in $SrCO_3$ precipitation. Similar to the speciation of C, the value of pH also influences the speciation of other ions such as inorganic phosphorus (iP). Moreover, the value of pH is also an indicator of the concentration of hydroxyl ions (OH^-) in a solution, which could potentially affect the equilibrium conditions through speciation hydroxide salts. Therefore, pH was chosen as a process condition to be studied.

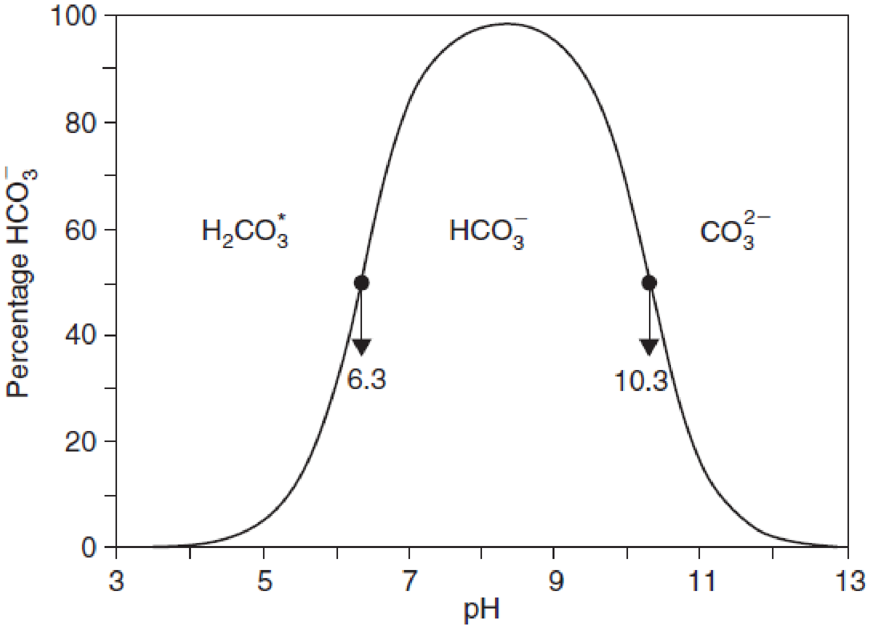

Figure 2: Variation in the percentage of HCO_3^- of the total aqueous carbonate ions with pH[71]

Temperature: Increasing the temperature (T) from 18 °C to 100 °C resulted in increasing the solubility of $SrCO_3$ from 11 mg/L to 650 g/L [72]. This clearly indicates that variation in T results in variation in the solubility of $SrCO_3$. The variation of T could also result in the variation of the dissolved CO_2 in a system. Increase in CO_2 results in formation of strontium bicarbonate ($Sr(HCO3)_2$) which increases the solubility of $SrCO_3$ [53]. Therefore, temperature was identified as a factor that could affect the precipitation of $SrCO_3$.

Pressure: Increase in pressure (P) can result in increased solubility of CO_2. While pressure itself may not have an effect on $SrCO_3$ precipitation, the variation in CO_2 levels accompanying the variation in pressure could influence equilibrium conditions.

Competitors

The driving force for the precipitation of $SrCO_3$ is the concentration of Sr^{2+} and CO_3^{2-} ions in the aqueous solution. Other ions present in aqueous solution may interact with these two ions to reduce their availability to form $SrCO_3$ and subsequently precipitate. The interaction could be reversible or irreversible. Interaction with other ions would result in a lower amount of $SrCO_3$ precipitated or if other ions interact with one another to form a different precipitate they could affect the purity the $SrCO_3$ precipitated. Therefore, it is important to identify which ions behave as competitors and what is the degree to which they can affect $SrCO_3$ precipitation. Apart from the competition, the nature of the ions could also introduce variability in terms of coprecipitation and/or indirectly acting as seeding material for $SrCO_3$ to precipitate. Calcium (Ca) and Barium (Ba) were considered as competitors due to similarities in properties with Sr^{2+}. Magnesium (Mg) was also considered as a potential competitor due to it being an alkaline earth metal as well. For the competitors of CO_3^{2-}, the anions of sulphate (SO_4^{2-}, as S) and inorganic phosphate (PO_4^{3-}, as iP) were considered due to the low solubility of their respective strontium salts. The effect of hydroxide salts (OH^-) could be evaluated through the variation of pH. Table 4 below presents the solubility of the matrix of the competitor ions shortlisted. It can be seen that amongst the possible salts that could be theoretically precipitated, $SrCO_3$ has one of the lowers solubilities, i.e. higher ease of precipitating.

Table 4: Solubility products of alkaline earth metals salts[53]

	CO_3^{2-}	SO_4^{2-}	PO_4^{3-}	OH^-
Sr^{2+}	1.1×10^{-10}	3.2×10^{-7}	1×10^{-31}	3.2×10^{-4}
Ca^{2+}	3.8×10^{-9}	2.5×10^{-5}	42×10^{-29}	5.5×10^{-6}
Ba^{2+}	4×10^{-10}	1.1×10^{-10}	6×10^{-39}	5×10^{-3}
Mg^{2+}	2.1×10^{-5}	-	1×10^{-13}	6×10^{-10}

Miscellaneous

The various factors identified above were all considered primarily due to their association with $SrCO_3$ precipitation. This category looks into factors that can be commonly expected or used to characterize a concentrate stream.

Ionic Strength: Ionic Strength (IS) refers to the collective concentration of all ions present in a solution. Concentrate streams usually tend to have a high IS due its concentrated nature. IS is used to calculate the activity coefficients of ions in a solution. These activity coefficients are used as correction factors to account for formation of aqueous complexes. The IAP of a salt is in turn calculated using the activity coefficients. Therefore, the variation in ionic strength of a solution could lead to a higher/lower value of SI which could influence whether a component precipitate or not. However, IS is not an independent parameter. It depends on the concentration of all the ions in an aqueous solution. Therefore, the effect of IS may be overshadowed by the effect of the ions that contribute to the IS. The true effect of IS can be evaluated only through variation of ions which do not have any other influence of the process.

Natural Organic Matter (NOM): Natural Organic Matter (NOM) refers to a broad range of organic compounds with varying composition and properties that occur naturally in the environment. NOM is an important characteristic that is used to assess the quality of water. The amount of NOM in the feed water and process steps prior to use of a filtration step would determine the final amount of NOM in the concentrate. The presence of NOM could lead to complexation with ions. The effect of the complexation would be dependent on the nature of the NOM as well as the ions being complexed. NOM could also be a source of variability for the amount of C in a solution.

2.3. OLI Simulations

Based on theoretical knowledge, factors that could have a potential positive or negative influence on $SrCO_3$ precipitation were shortlisted. To verify the effect of the shortlisted factors OLI simulations were performed. These simulations were performed to study the effects of the factors in a general setting and not specifically to what could be observed in concentrates. The aim of these simulations was to verify whether the presence of and/or variation in a factor could impact $SrCO_3$ precipitation in terms of either:

- Amount of $SrCO_3$ precipitated
- Purity of $SrCO_3$ precipitated

These two indicators encompass both, the qualitative and quantitative aspects of $SrCO_3$ precipitation. To study the effects of the shortlisted factors, a solution with a fixed and equal concentrations of Sr and C was created. Four different values of fixed concentrations were chosen, 0.1 mM, 1 mM, 10 mM and 100 mM. The reason for choosing these fixed concentrations was to confirm whether the effect of a factor was limited to only certain concentration ranges or was it applicable across all concentration ranges.

While the effect of the process conditions was evaluated individually, the rest of the factors were evaluated while varying the pH simultaneously. This was done as it was expected that the effect of certain factors would be dependent on the value of pH. The effect of all ions considered were analysed by varying their concentration between zero to two times of the chosen fixed value. By doing so, if a factor had an effect, the required concentration of the ion to see the effect could also be estimated.

As for the miscellaneous factors, the effect of ionic strength was evaluated through the addition and variation of sodium nitrate ($NaNO_3$). To evaluate the effect of natural organic matter (NOM), the form of NOM had to be fixed. For this study, the effect of NOM was evaluated through formic, acetic and propionic acid. It would have been more ideal to represent NOM through humic or fulvic acids but since these couldn't be simulated using OLI, they were not considered. The design table for these OLI simulations can be seen in Table 5 and the range of values for the different simulations can be seen in Table 6.

Table 5: Design table for OLI simulations performed to identify relevant factors.
"F" refers to the variable have a fixed value for the simulation. "V" refers to a variation of the variable in the simulation. The range of variables can be referred to from Table 6.

	Value in Simulation											
	pH	T	P	Sr	C	Ca	Ba	Mg	S	P	IS	NOM
Process Conditions												
pH	V	-	-	F	F	-	-	-	-	-	-	-
T	-	V	-	F	F	-	-	-	-	-	-	-
P	-	-	V	F	F	-	-	-	-	-	-	-
Driving Force												
Sr	V	-	-	V	F	-	-	-	-	-	-	-
C	V	-	-	F	V	-	-	-	-	-	-	-
Competitors												
Ca	V	-	-	F	F	V	-	-	-	-	-	-
Ba	V	-	-	F	F	-	V	-	-	-	-	-
Mg	V	-	-	F	F	-	-	V	-	-	-	-
S	V	-	-	F	F	-	-	-	V	-	-	-
P	V	-	-	F	F	-	-	-	-	V	-	-
Miscellaneous												
IS	V	-	-	F	F	-	-	-	-	-	V	-
NOM	V	-	-	F	F	-	-	-	-	-	-	V

Table 6: Range of factors studied using OLI simulation

	Range			
Process Conditions				
pH	0 - 14			
T	-20 °C - 120°C			
P	1 atm – 60 atm			
Driving Force				
Sr	0.1 mM	1 mM	10 mM	100 mM
C	0.1 mM	1 mM	10 mM	100 mM
Competitors				
Ca	0 – 0.2 mM	0 – 2 mM	0 – 20 mM	0 – 200 mM
Ba	0 – 0.2 mM	0 – 2 mM	0 – 20 mM	0 – 200 mM
Mg	0 – 0.2 mM	0 – 2 mM	0 – 20 mM	0 – 200 mM
S	0 – 0.2 mM	0 – 2 mM	0 – 20 mM	0 – 200 mM
P	0 – 0.2 mM	0 – 2 mM	0 – 20 mM	0 – 200 mM
Miscellaneous				
IS[3]	0 – 0.2 mM	0 – 2 mM	0 – 20 mM	0 – 200 mM
NOM	0 – 0.2 mM	0 – 2 mM	0 – 20 mM	0 – 200 mM

A detailed stepwise procedure on how the simulations were performed using OLI is presented in Appendix 9.2. The interpretation for how the performed simulations were evaluated is discussed below using one set of simulations carried out (at Sr, C = 1 mM) for context. The outcomes for the other simulations (at Sr, C = 0.1 mM, 10mM and 100 mM) is provided in Appendix 9.2. To fully understand how the OLI simulations were performed and evaluated, some basic points need to be taken into consideration:

1. OLI software does not make direct use of ionic concentration for its calculation. Ionic compositions can be converted to a form with which it can perform calculations. Therefore, for these simulations the manipulation of ions has been carried out via their sodium or chloride salts.
2. Specifically, for temperature related simulations, the results at temperature below the one where ice is formed is not reliable and is not considered for this study.
3. The collective group of all the solid phases forming at equilibrium is labelled as “Dominant Solids”. The components of this “Dominant Solids” can be selected individually or collectively. It is also possible to omit certain solid phases from being formed/calculated. For these simulations no restrictions were provided in terms of which phases/components were allowed to precipitate.
4. Co – precipitation is not taken into account for the simulations as it is not a part of the current software. All solids precipitated were pure phases.
5. Calculations in OLI are carried out for a single point of defined variables/components. A ”Survey” simply refers to a group of such single point calculations where the step size for the next value of the defined variables/components is provided.

Discussed below is the outcome of one of the four sets of simulations carried out to identify the relevant factors. The graphical outcomes for the rest of the three sets of simulations are provided in Appendix 9.2 and can be interpreted in the same fashion as the one discussed below.

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[3] IS is varied through $NaNO_3$

Process Conditions

- pH: The effect of variation of pH on amount of $SrCO_3$ precipitated can be observed in Figure 3. It can be seen that $SrCO_3$ precipitation is observed in the alkaline pH range. Below a pH of 7 no $SrCO_3$ precipitation is observed. Below a particular pH value, inorganic carbon speciates as HCO_3^- or dissolved CO_2. This prevents the formation of $SrCO_3$ as there are no CO_3^{2-} ions. This is indicative of the fact that the pH of a solution is needed to be above a certain value in order for $SrCO_3$ to precipitate. Increasing the pH from a neutral range to alkaline increases the $SrCO_3$ precipitated substantially. Further increase of pH within the alkaline range does not lead to a major increase in the amount of $SrCO_3$ precipitated. However, when the pH is increased to an extreme alkaline range (>12), the amount of $SrCO_3$ precipitated decreases as some amount of Sr is made unavailable due to speciation as $SrOH^+$.

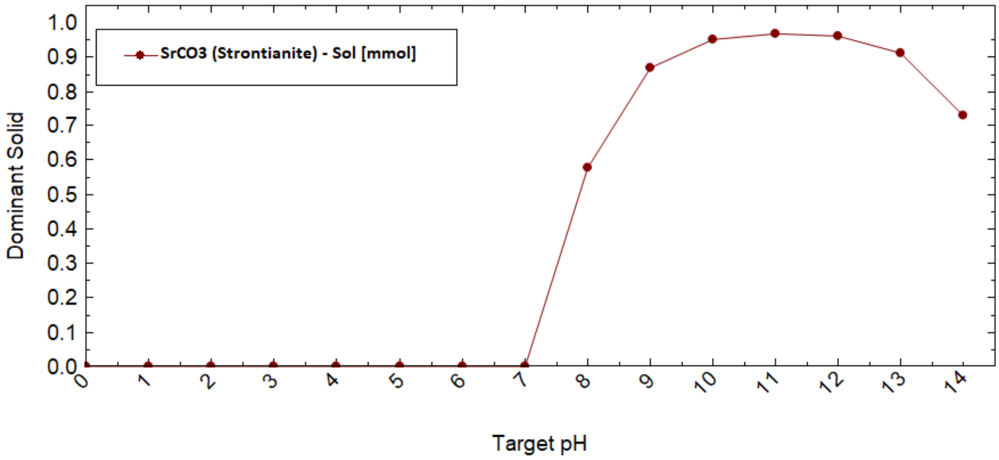

Figure 3: Variation in amount of $SrCO_3$ precipitate formed versus the variation in pH at Sr, C = 1 mM

- Temperature: The effect of variation of temperature (T) on the amount of $SrCO_3$ precipitated can be seen in Figure 4. It is observed that with the increase in temperature the amount of $SrCO_3$ precipitating follows a decreasing trend. However, this decrease is close to only 10% of the total Sr present in the solution. Therefore, while the solubility of $SrCO_3$ is increasing with T, the increase is only minor. At T above 100 °C all the Sr is precipitated as $SrCO_3$ as under equilibrium conditions all the water has turned into vapour phase.

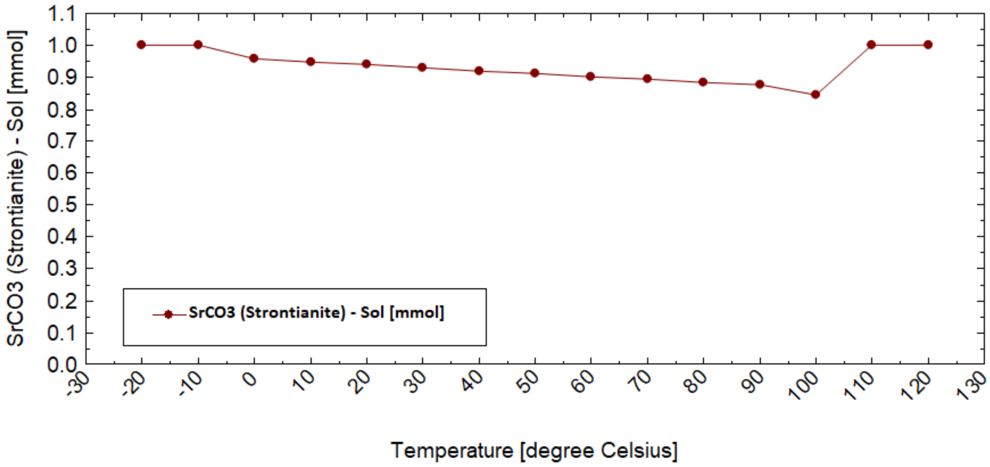

Figure 4: Variation in amount of $SrCO_3$ precipitate formed versus the variation in T at Sr, C = 1 mM

- Pressure: From Figure 5 it can be seen that the variation of pressure (P) does not impact the amount of $SrCO_3$ precipitated. This indicates that in a closed system the amount of $SrCO_3$ precipitated is independent of the variation in P.

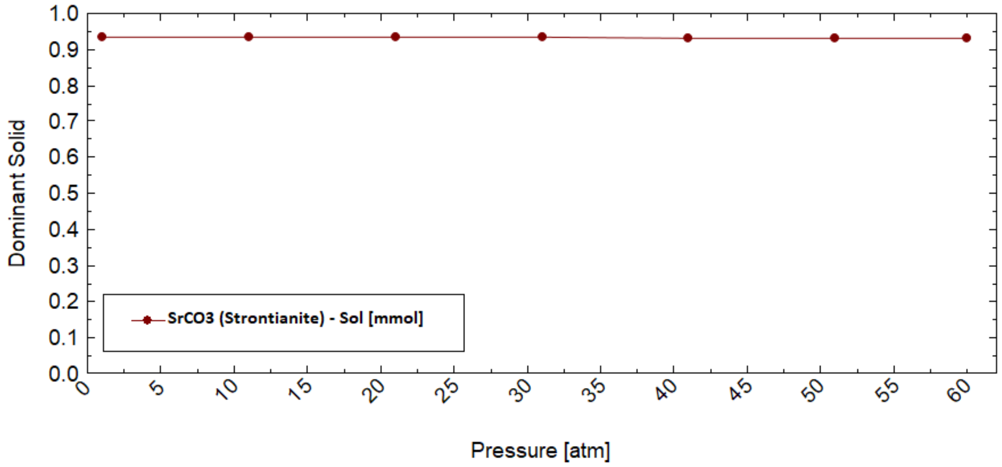

Figure 5: Variation in amount of $SrCO_3$ precipitate formed versus the variation in P at Sr, C = 1 mM

Driving Force

- Strontium concentration: As seen in Figure 6, the amount of $SrCO_3$ precipitated increases linearly with the amount of Sr added to the solution and is limited by the amount of C available. It can also be seen that while the amount of Sr influences the amount of $SrCO_3$ being precipitated, the latter also depends on the value of pH.

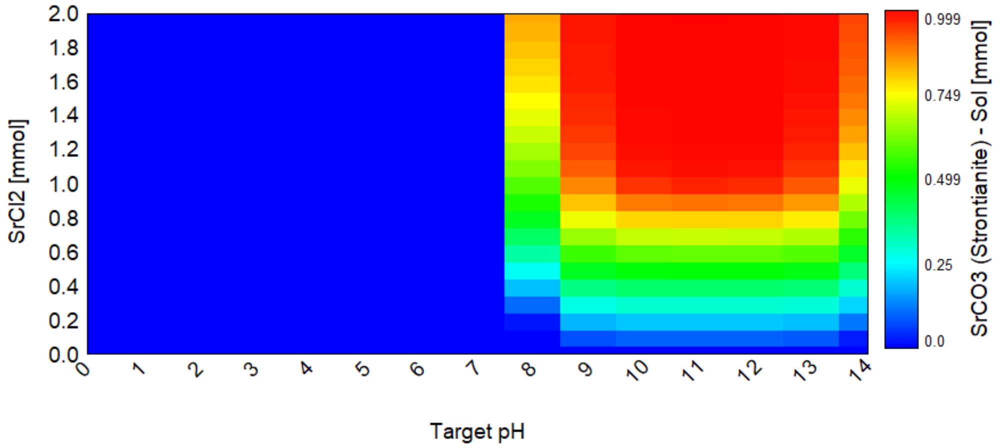

Figure 6: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, Sr at Sr, C = 1 mM

- Inorganic carbon concentration: Similar to Sr, a linear increase in the amount of $SrCO_3$ precipitated can be observed when increasing the value of C (Figure 7). This again is limited by the amount of Sr available in the solution and its impact can be enhanced by increasing the pH.

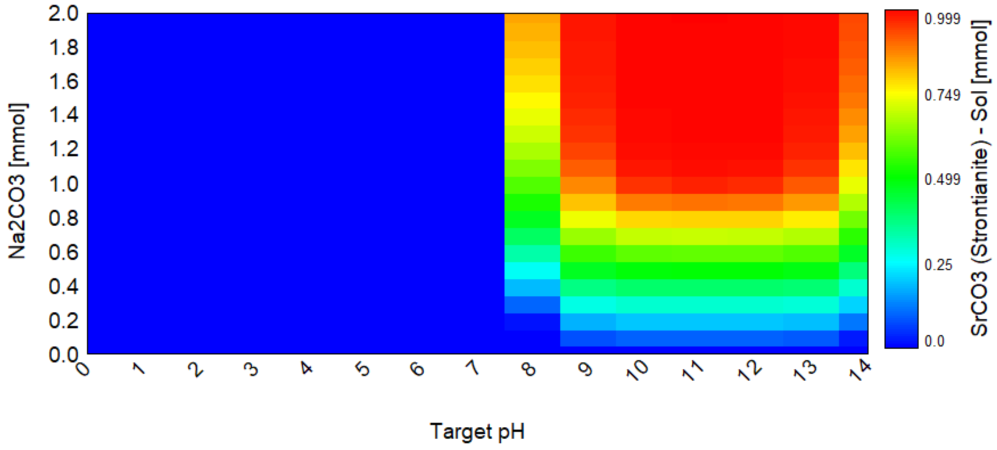

Figure 7: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, C at Sr, C = 1 mM

Competitors

- Calcium concentration: Figures 8,9 and 10 represent the variation in the precipitates being formed when the amount of calcium (Ca) and value of pH in the solution are being varied. An increase in Ca results in lower amount of $SrCO_3$ being precipitated. At the same time $CaCO_3$ precipitation is observed which could act as an impurity. At higher pH, precipitation of $Ca(OH)_2$ is expected which also acts as an impurity. It can be seen that the presence (and variation) of Ca in an aqueous solution impact the quantity and quality of $SrCO_3$ being precipitated.

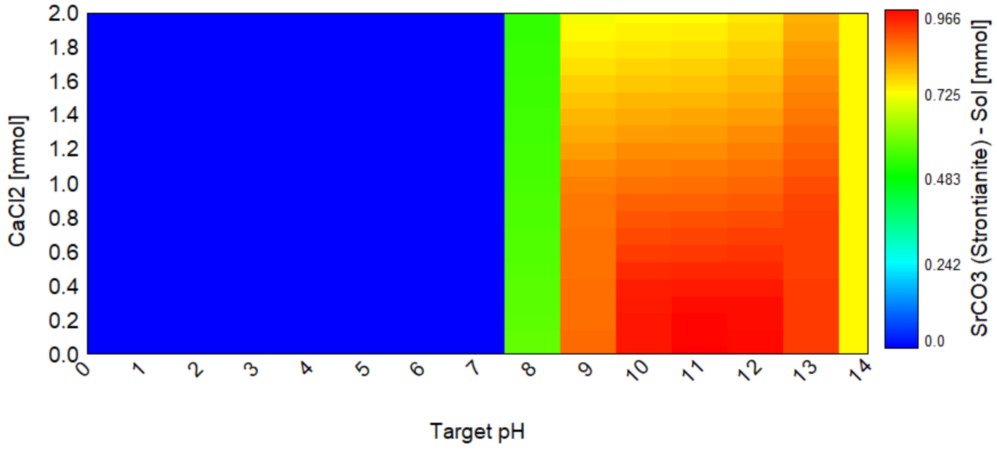

Figure 8: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, Ca at Sr, C = 1 mM

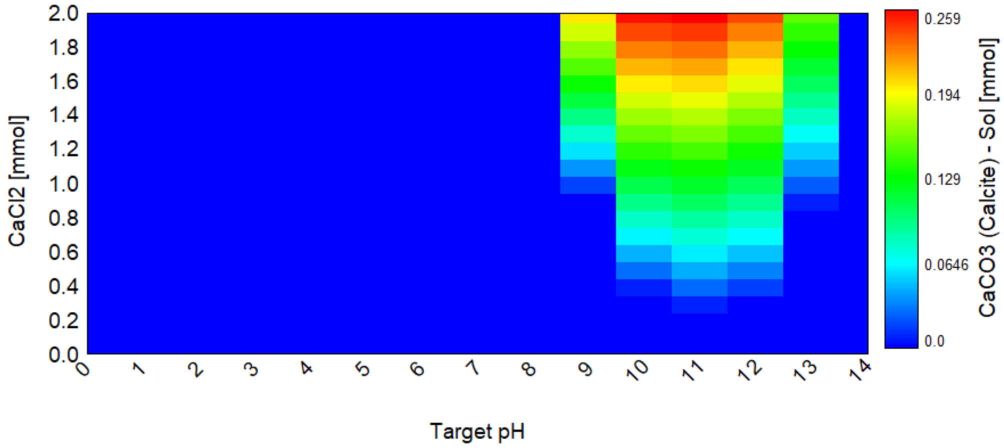

Figure 9: Variation in amount of $CaCO_3$ precipitate formed versus the variation of pH, Ca at Sr, C = 1 mM

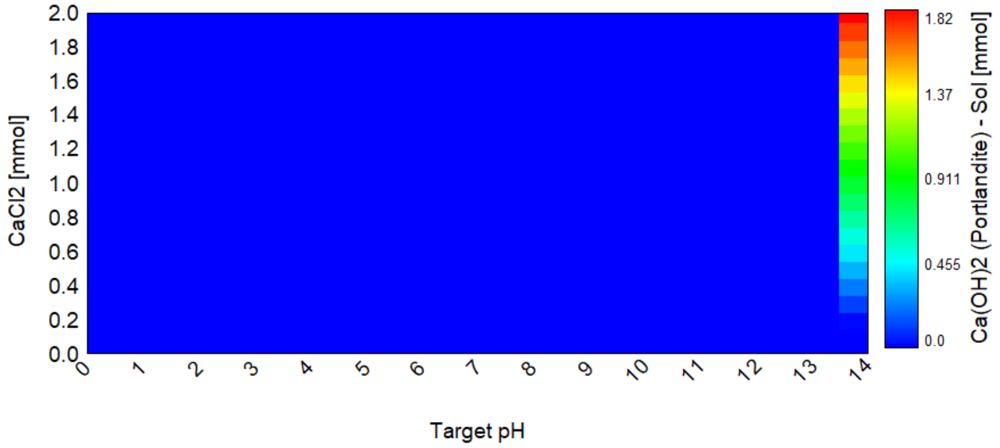

Figure 10: Variation in amount of $Ca(OH)_2$ precipitate formed versus the variation of pH, Ca at Sr, C = 1 mM

- Barium concentration: Similar to the effect of Ca, the presence of barium (Ba) affects both the quality and quantity of $SrCO_3$ precipitated (Figure 11, 12). Ba can form $BaCO_3$ which could act as an impurity for the $SrCO_3$ precipitated while at the same time reducing the total amount of C available for Sr to precipitate as $SrCO_3$.

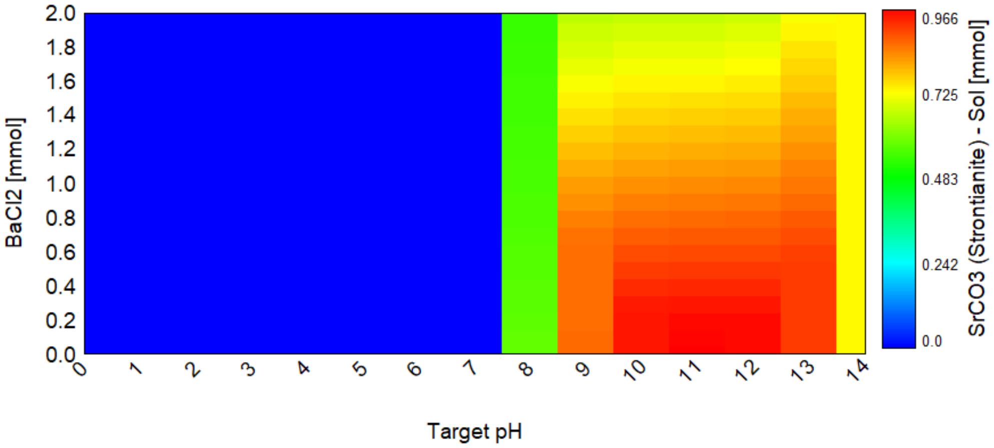

Figure 11: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, Ba at Sr, C = 1 mM

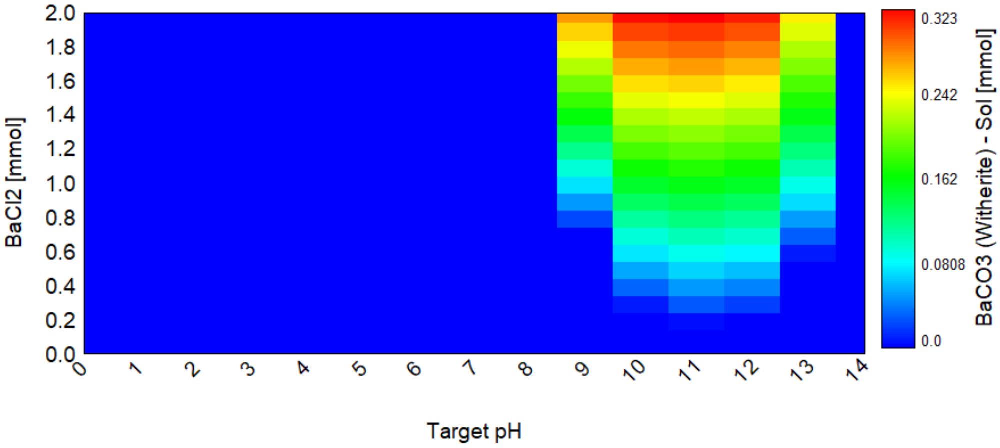

Figure 12: Variation in amount of $BaCO_3$ precipitate formed versus the variation of pH, Ba at Sr, C = 1 mM

- Magnesium concentration: As seen in Figure 13, the presence of Magnesium (Mg) itself doesn't seem to have an impact on the amount of $SrCO_3$ precipitated. However, beyond a certain pH range Mg precipitates as $Mg(OH)_2$ (Figure 14) which would act as an impurity for the $SrCO_3$ precipitated.

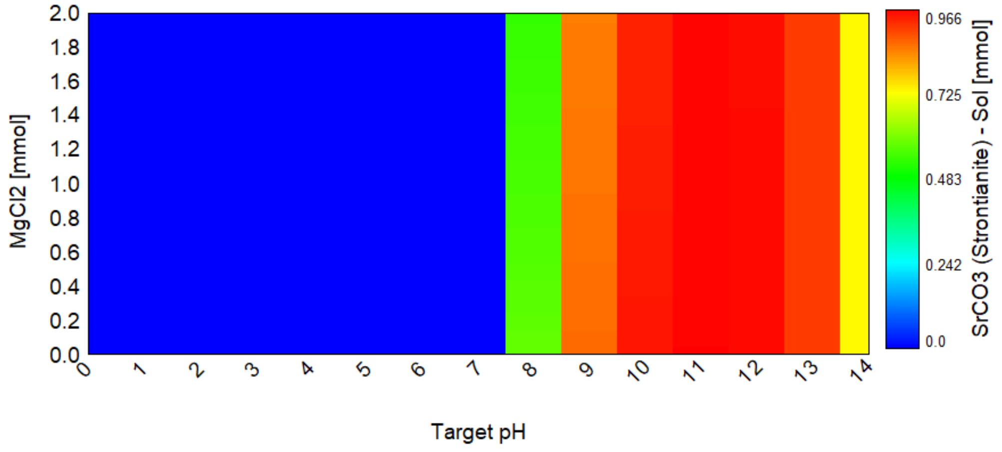

Figure 13: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, Mg at Sr, C = 1 mM

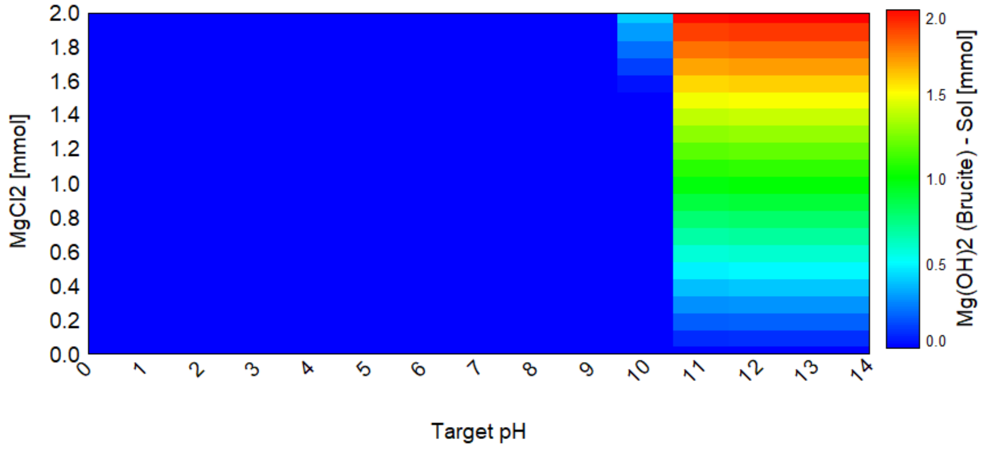

Figure 14: Variation in amount of $Mg(OH)_2$ precipitate formed versus the variation of pH, Mg at Sr, C = 1 mM

- Inorganic sulphur concentration: The effect of inorganic sulphur (S) (Figure 15, 16) seems to be dependent on the pH of the solution. At an alkaline pH the amount of $SrCO_3$ seems to remain constant irrespective of the amount of S in the solution. However, at an acidic and neutral pH, substantial precipitation of $SrSO_4$ was observed.

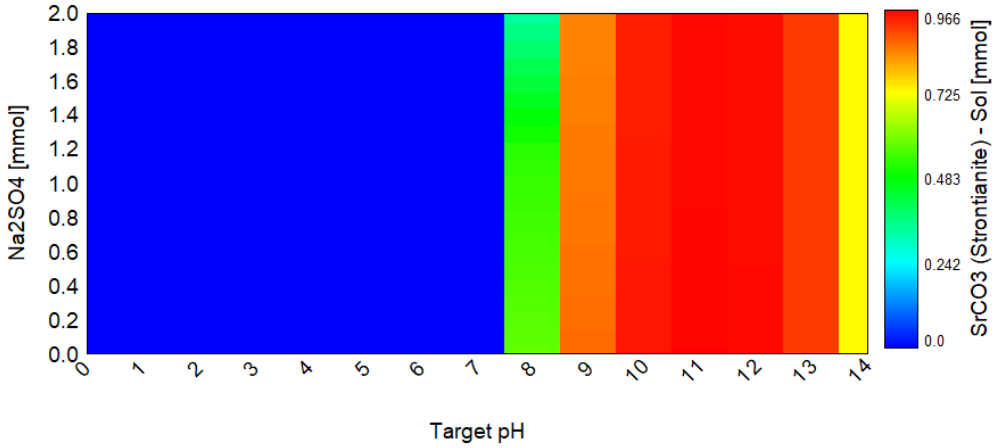

Figure 15: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, S at Sr, C = 1 mM

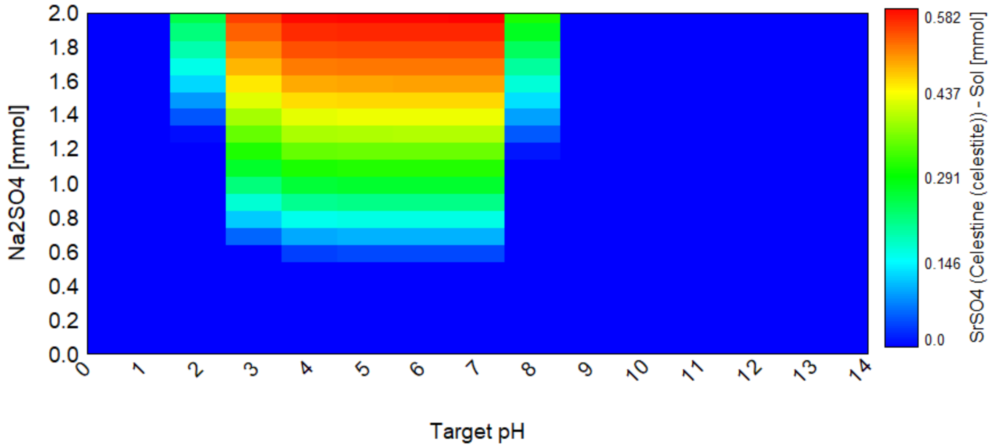

Figure 16: Variation in amount of $SrSO_4$ precipitate formed versus the variation of pH, S at Sr, C = 1 mM

- Inorganic phosphorus concentration: As seen in Figure 17, the presence and/or variation of inorganic phosphorus (iP) in the aqueous solution did not influence the amount of $SrCO_3$ precipitating. No other precipitates were formed either indicating that iP may not play a role as a competitor in the precipitation of $SrCO_3$.

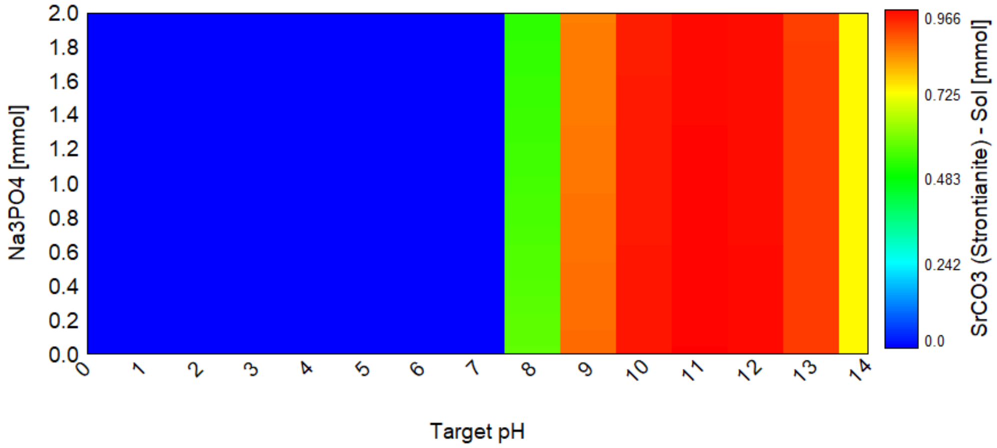

Figure 17: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, iP at Sr, C = 1 mM

Miscellaneous

- Ionic Strength: As seen in Figure 18, the variation in ionic strength (via $NaNO_3$) does not result in any variation of $SrCO_3$ precipitating.

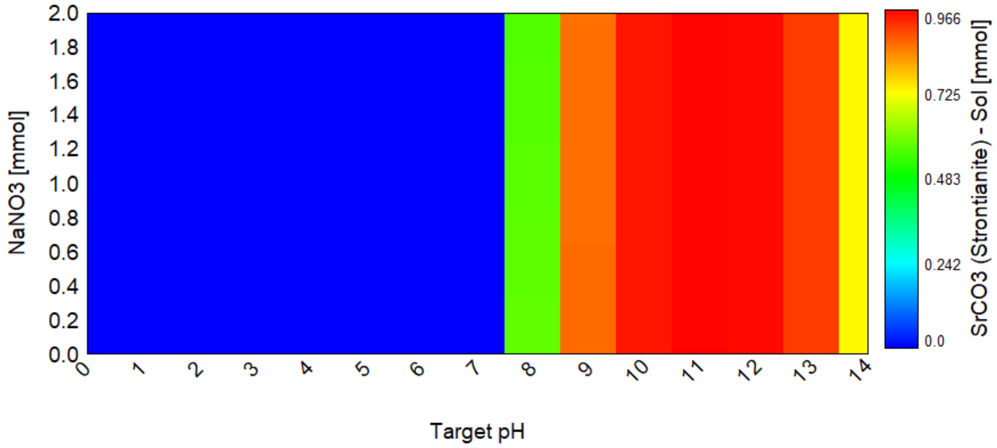

Figure 18: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, $NaNO_3$ at Sr, C = 1 mM

- Natural Organic Matter: The effect of variation of formic acid, acetic acid and propionic acid on the amount of $SrCO_3$ precipitated can be observed in Figure 19, 20 and 21 respectively. The variation of these three organic acids did not show any impact on the precipitation of $SrCO_3$ in terms of either quality or quantity

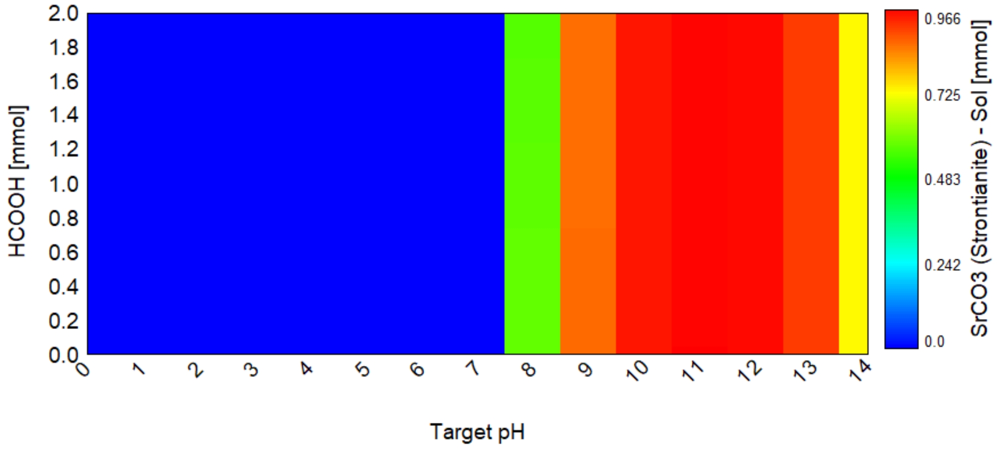

Figure 19: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, Formic Acid at Sr, C = 1 mM

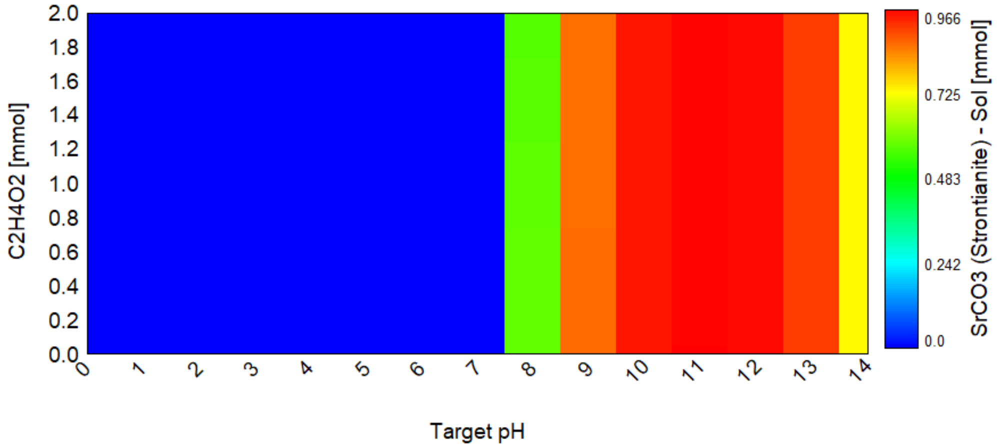

Figure 20: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, Acetic Acid at Sr, C = 1 mM

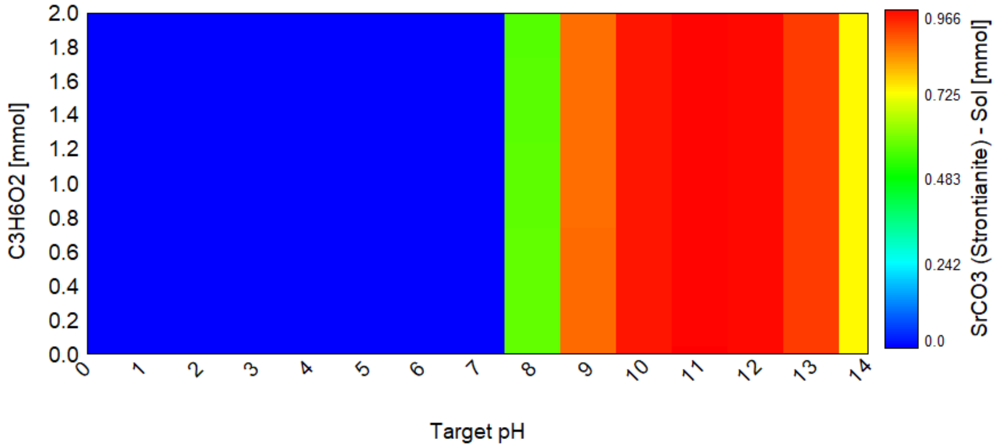

Figure 21: Variation in amount of $SrCO_3$ precipitate formed versus the variation of pH, Propionic Acid at Sr, C = 1 mM

Table 7 below summarizes the effect of factors on $SrCO_3$ precipitation based on the simulations run.

Table 7: Summary of observed effects of identified factors on $SrCO_3$ precipitation

	Observable Effect			
	0.1 mM	**1 mM**	**10 mM**	**100 mM**
Process Conditions				
pH	✓	✓	✓	✓
T	✓	x	x	x
P	x	x	x	X
Driving Force				
Sr	✓	✓	✓	✓
C	✓	✓	✓	✓
Competitors				
Ca	x	✓	✓	✓
Ba	x	✓	✓	✓
Mg	✓	✓	✓	✓
S	x	✓	✓	✓
iP	x	x	x	x
Miscellaneous				
IS	x	x	x	x
NOM	x	x	x	x

Chapter 4.2 which deals with the selection of factors for the experimental design takes into consideration the observed effect of different factors as seen in Table 7.

3. Quality of PWN concentrate

Chapter Summary: **This chapter looks into multiple aspects of the reverse osmosis concentrate created as a waste stream during drinking water production at the water treatment facility of PWN located in Heemskerk. This concentrate is used as a real world example to understand what kind of challenges could be expected and needed to be addressed in order to successfully recovery Sr as $SrCO_3$ from industrial concentrate streams. The relevant details pertaining to the production and quality of the concentrate are presented. The manipulation of concentrate quality via variation in process conditions as a method to enhance $SrCO_3$ recovery is also discussed.**

3.1. Production scheme

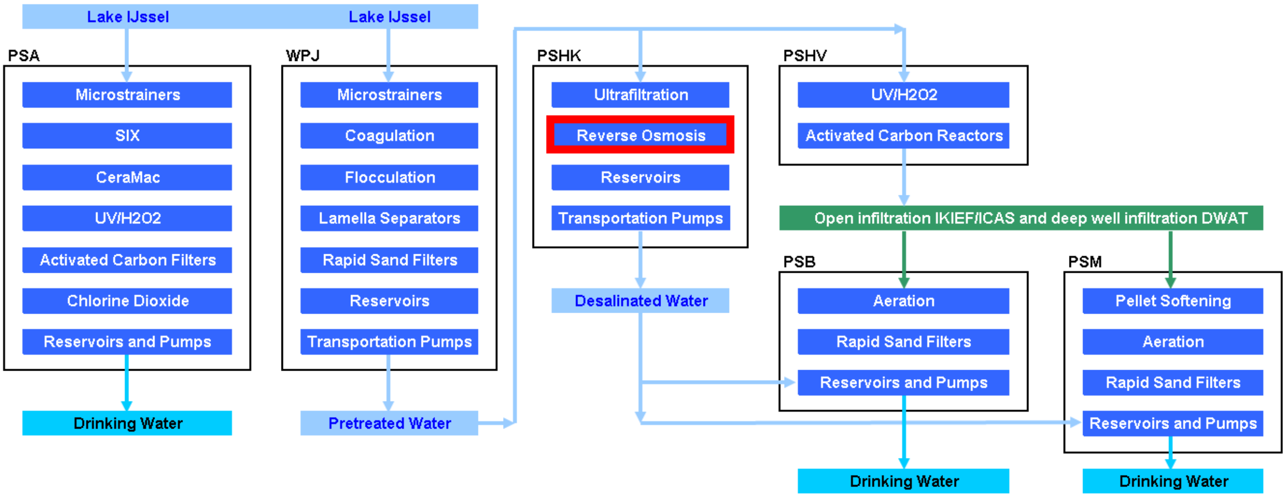

Figure 22: Drinking water production scheme, PWN

The production scheme for drinking water at PWN can be seen in figure 22 above[4]. The concentrate to be focussed upon in this section is produced at the “Reverse Osmosis” (RO) stage, demarcated in red in the figure above. The RO stage operates at 80% recovery producing concentrate at a rate of 504 m^3/h. Currently, the produced concentrate is discharged as per defined regulations.

3.2. Concentrate characteristics

The quality of the concentrate produced can be seen in Table 8 below. The data represents measurements made in 2019 only. Since different properties were measured with different frequency, the number of data points used to calculate average and standard deviation (S.D.) can be seen under “n”. Lastly data/characteristics not measured are marked as “N.A”. The quality of the feed to the RO and also the quality of the overall feed can be seen in Appendix 9.3.

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[4] Apart from feed from Lake Ijssel, another feed stream is sourced from the Rhine (not shown in figure)

Table 8: Quality of concentrate produced at PWN[5]

Parameter	Units	Concentrate		
		Average	**S.D.**	**n**[6]
Cations				
Na^+	*mg/L*	371	63	11
Ca^{2+}	*mg/L*	282	47	11
Mg^{2+}	*mg/L*	?	-	-
Sr^{2+}	*mg/L*	1.91	0.12	11
Ba^{2+}	*mg/L*	0.21	0.02	11
Iron	*µg/L*	N.A.	-	-
K^+	*mg/L*	N.A.	-	-
Al^{3+}	*mg/L*	N.A.	-	-
Anions				
Cl^-	*mg/L*	665	88	48
HCO_3^-	*mg/L*	645	85	11
SO_4^{2-}	*mg/L*	287	21	48
NO_3^-	*mg/L N*	0.92	0.23	96
CO_3^{2-}	*mg/L*	0	0	11
PO_4^{3-}	*mg/L P*	N.A.	-	-
Others				
pH	*-*	8.08	0.04	48
Temperature	*°C*	11.50	0.58	59
Conductivity	*mS/m*	306.64	24	11
CO_2	*mg/L*	N.A.	-	-
DO	*mg/L O_2*	8.88	1.7	11
TOC	*mg/L*	N.A.	-	-
Total hardness	*mmol/L*	N.A.	-	-
COD	*mg/L O_2*	37.19	3.29	48
Silicate	*mg/L Si*	N.A.	-	-
DCT	*cel/mL*	37903	21178	3
AOC	*mg/L C*	0.02	0.002	3
ATP	*ng/L*	2.52	0.91	3

While the majority of the relevant data is present, Mg^{2+} concentration in the concentrate is missing. Since the presence and/or variation of Mg^{2+} concentration could have an impact on the behaviour of the solution, it was important to obtain this value. To obtain this value, the RO process was simulated using IMSDesign[7]. The quality of the simulated concentrate in comparison to the actual quality of the concentrate can be seen in Table 9.

As per the IMSDesign simulations, the value of Mg^{2+} in the concentrate is 67.2 mg/L. This value was considered representative of the actual concentration in the brine on the basis of the following two reasons:

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[5] This information was provided via one of the internal documents from PWN. The relevant data has been extracted and presented

[6] Available measurements were first averaged out on a monthly basis and then on an annual basis

[7] Refer to attached supporting file named "PWN UF Effluent – 218"

- The values for the divalent cations obtained via simulation are in proximity with the actual measured values in the concentrate.
- The concentration factor of all the components (except Na^+ and Cl^-) are all approximately 5 corresponding to a recovery of 80%. The concentration factor for Mg^{2+} from the simulation also comes to around 5 thereby following the behaviour as would be expected.

The difference observed in the values for Na^+ and Cl^- can be attributed to the fact that IMSDesign uses these two ions to maintain charge balance and subsequently the difference in Na^+ and Cl^- concentrations can explain the variation in the conductivity value. The variation in pH can be explained by the use of a specific chemical anti-scalant during the RO operations[8] which could not be reproduced in the IMSDesign simulations.

Table 9: Concentrate quality as per IMSDesign simulation in comparison to measured data

Parameter	Units	Concentrate (RO) Measurements	Concentrate (RO) IMSDesign	Difference (%)[9]
Cations				
Na^+	mg/L	370.29	475	27 %
Ca^{2+}	mg/L	282.14	285	0.8 %
Mg^{2+}	mg/L	?	67.2	-
Sr^{2+}	mg/L	1.91	2.03	6 %
Ba^{2+}	mg/L	0.21	0.206	2.4 %
Anions				
Cl^-	mg/L	665.25	847	26.5 %
HCO_3^-	mg/L	644.57	663	0.33 %
SO_4^{2-}	mg/L	286.19	286	0.46 %
CO_3^{2-}	mg/L	0	18.3	-
NO_3^-	mg/L N	0.92	N.A.	-
Others				
pH	-	8.08	8.57	6.1%
Temperature	°C	11.5	-	-
Conductivity	mS/m	306.64	434.4	42%
CO_2	mg/L	N.A.	2.98	-

3.3. Pre-treatment of Concentrate

Based on the measured quality of the concentrate as seen in Table 9, it is evident that Sr^{2+} and HCO_3^- ions are present, making $SrCO_3$ precipitation a realistic possibility. However, along with these two ions, other ions such as Ca^{2+}, SO_4^{2-} etc. are present and are in much larger concentrations. This makes it necessary to separate the desirable ions (Sr^{2+} and HCO_3^-) from the rest in order to have suitable conditions for the recovery of $SrCO_3$.

This subsection proposes a scheme that could be used to separate Sr ions from the rest. As one of the themes for this study is resource recovery, the unwanted components are attempted to be

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[8] Information provided verbally by PWN engineers

[9] Calculated as (|Measurements – IMSDesign|)/ Measured Value x 100

recovered at the same time rather than just be separated and removed. This scheme could be considered as a pre-treatment step to allow for the recovery of $SrCO_3$ from the concentrate. The proposed pre-treatment is based only on the variation of process conditions: pH, Temperature (T) and Pressure (P) and explored through OLI simulations. The general procedure followed for the development of this scheme is explained through the steps below:

a. The effect of variation of pH, T and P on the concentrate was observed through six different simulations. First, the three factors were varied individually and next, they were varied simultaneously (pH – T, pH – P and T – P). The factors were varied simultaneously to identify if the effect of one process condition depended on the value of another process condition. Table 10 represents the simulations run for identification of recovery targets. If not varied, the value of the factor was kept at default i.e. value observed in the feed.

Table 10: Set of simulations run to identify target for recovery as means of pre-treatment

	pH	**T**	**P**
Range	1 - 14	-20°C - 120°C	1 atm – 100 atm
Step Size	1	10°C	10 atm
Survey			
pH	✓	x	x
T	x	✓	x
P	x	x	✓
pH – T	✓	✓	x
pH – P	✓	x	✓
T – P	x	✓	✓

b. Based on performed simulations, the different precipitates being formed were analysed. The precipitate being formed in the highest amount was considered as the main precipitate and the rest of the precipitating components were considered as impurities for the main precipitate.

c. The main precipitate would then be the target for recovery. The graphical output of the six simulations were analysed manually. A rough estimate for a range for pH, T and P would be derived where the highest amounts of the main precipitate would be expected to precipitate. Within this estimated range the required simulations would be repeated in more detail (higher resolution).

d. Data points from the more detailed simulations would be extracted for comparison. The data points would be evaluated on the basis of three separate criteria.
   (i) Criteria A: Product Purity
   (ii) Criteria B: Absolute amount of precipitate formed
   (iii) Criteria C: Environmental footprint

$$\text{Product Purity (\%)} = \frac{\text{Weight of main precipitate (mg)}}{\text{Weight of all precipitates (mg)}} \times 100 \quad \text{Eq. (6)}$$

Criteria A was evaluated based on Equation 6. Environmental footprint was evaluated based on the expected chemical consumption required for pH adjustment and expected energy consumption required for maintaining the desired temperature and pressure. The data points that would satisfy these three criteria the best individually would be considered as the most suitable options for recovering the main precipitate. The decision to evaluate on the basis of these three criteria was a subjective decision. These three criteria cover the qualitative, quantitative and environmental aspects of decision making. The choice for the final/ultimate process condition out of the three most suitable options was also a subjective decision. The choice which seemed more reasonable relative to the other two was considered as the value of the process conditions at which the main precipitate would be recovered. To make the choice, consideration was given on how it would impact the steps downstream and also its impact of precipitation of $SrCO_3$.

e. At the final chosen process conditions, the precipitates formed were separated from the aqueous stream. The precipitate free aqueous stream was then subject to the same investigative procedure (steps a. to d.).

A few additional points need consideration when evaluating this pre-treatment scheme.

- The pre-treatment scheme is based entirely on final equilibrium conditions. The kinetics of the precipitation along with the economic suitability of a choice is not considered.

- Each of the three criteria for decision making are evaluated independent of each other. A better alternative to this would be evaluating each data point for all three criteria and choose the data point which fits all three criteria the best simultaneously. For this to take place, an in-depth decision making protocol needs to be made, for e.g. Salt “ABC” needs to be recovered within a purity range of “X%” – “Y%”.

- “Criteria C” i.e. the Environmental Footprint is evaluated based on the amount of chemicals required for the variation of pH and the energy consumption associated with the chosen temperature and pressure. The impact of chemical consumption on the environmental footprint is bound to be significantly different from the impact of energy consumption and is dependent on a number of factors (for e.g. availability of waste heat). To make the choice for the process conditions based on the lowest environmental footprint, weights need to be first assigned for each unit of chemical consumption and each unit of energy consumption.

- The outcomes selected represent the area where the most suitable process conditions lie in the vicinity of. The exact data points are expected to vary at least slightly.

Based on the procedure detailed above a pre-treatment scheme was developed. The overview of this pre-treatment scheme is shown in Figure 23. Each step of the pre-treatment is discussed below[10]. The pre-treatment scheme is based on 1 L of the concentrate i.e. all findings are per litre of concentrate.

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[10] Refer to attached supporting file named “Pre – treatment of Concentrate”

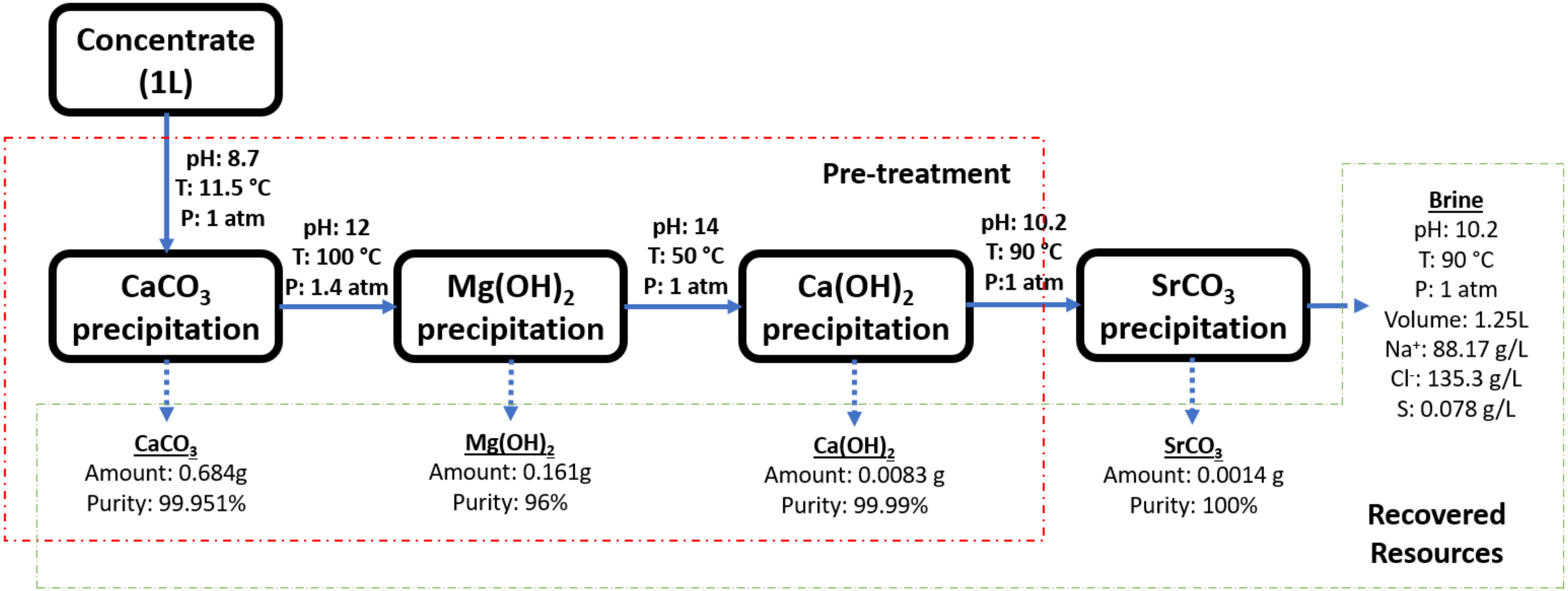

Figure 23: Summary of pre-treatment scheme along with all resources recovered

3.3.1. Pre – treatment Step 1: Recovery of $CaCO_3$

Table 11: Concentration of different elements in the concentrate

Element	Total Concentration (mg/L)
Na	515
Ba	0.21
Ca	282.1
Mg	67.2
Sr	1.91
C	127
S	95.5
N	0.92
Cl	679

The composition of the concentrate is presented in Table 11. To identify the target for recovery, six simulations as described in Table 10 were run on the concentrate. Figure 24 – 29 represent the outputs of these simulations.

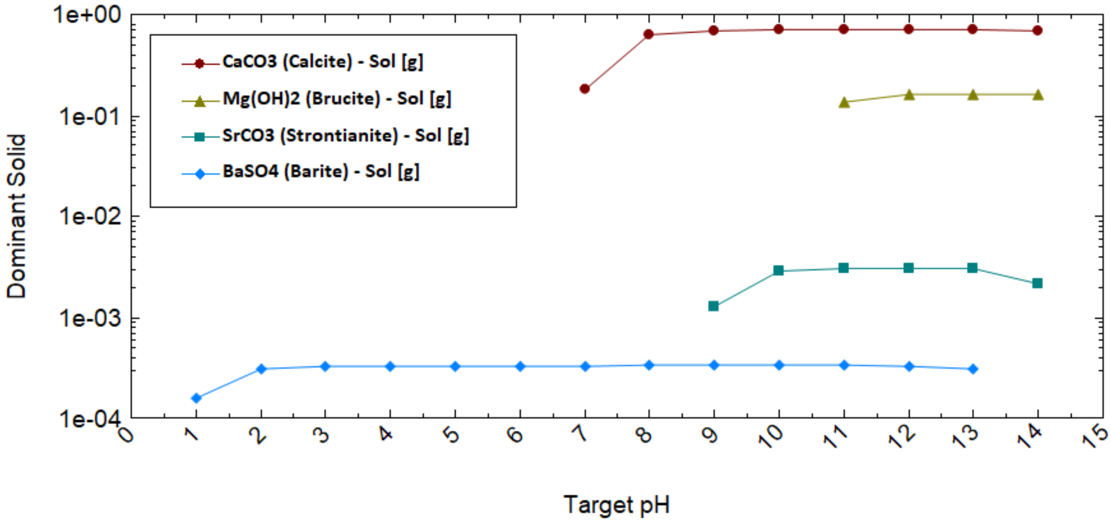

Figure 24: Precipitates formed in concentrate subject to different pH value

From Figure 24 it can be seen that if the concentrate is subject to different pH values, $CaCO_3$, $Mg(OH)_2$, $SrCO_3$ and $BaSO_4$ are expected to precipitate. It can also be observed that the value of pH influences the amount of precipitate formed.

The temperature survey (Figure 25) indicates that the variation of temperature (at the given pH, i.e. 8.08) does not result in substantial changes to the amount of precipitates being formed. At 0 °C ice is being formed indicating that the predictions below that temperature may not be reliable. The precipitate being formed in the highest quantity is $CaCO_3$. On comparison with the pH survey it can be seen that the pH value is not high enough for $SrCO_3$ precipitation. However, $SrCO_3$ precipitation can be observed when the temperature is varied. This indicates that along with pH, T also has an effect on $SrCO_3$ precipitation under these conditions.

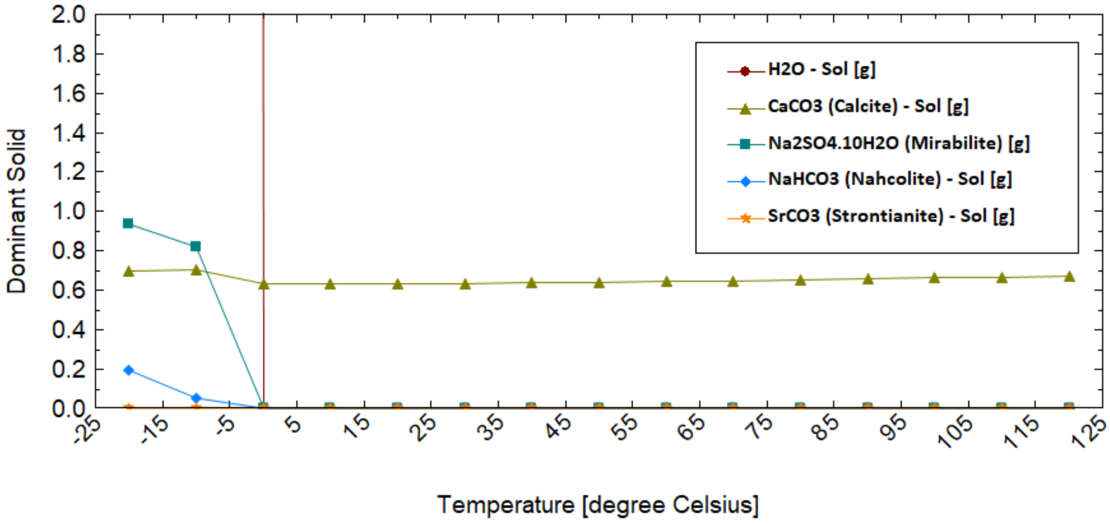

Figure 25: Precipitates formed in concentrate subject to different T value

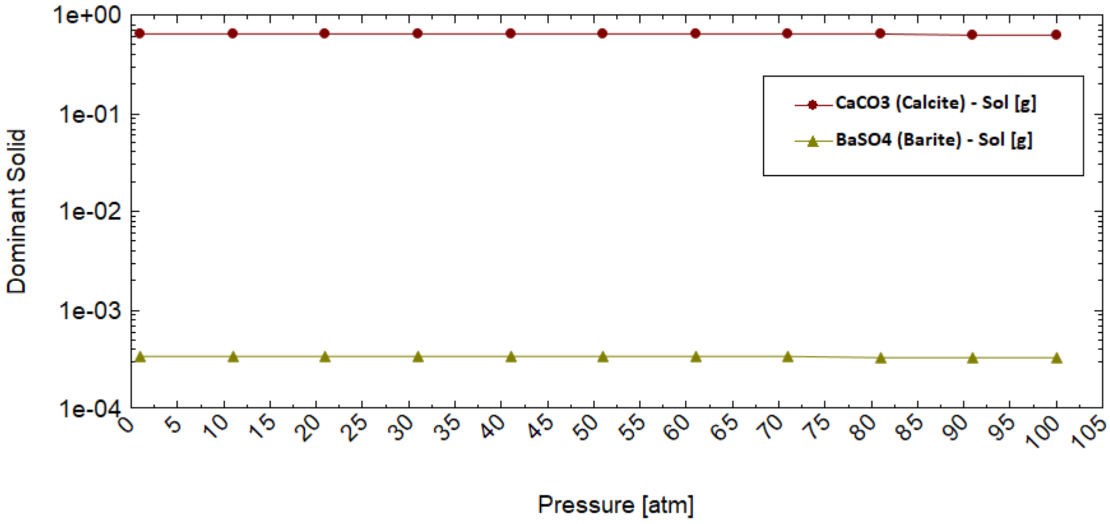

Figure 26: Precipitates formed in concentrate subject to different P value

The simulated pressure survey (Figure 26) indicates that the variation in pressure (at the given pH) does not impact the amount of each individual precipitate being formed. Precipitation of $SrCO_3$ and $Mg(OH)_2$ is not observed as the pH is not sufficiently high for the same. From the individual surveys it is evident that $CaCO_3$ is the solid being precipitated in the largest quantity. Therefore, for the first pre-treatment step, $CaCO_3$ was chosen as the target/main precipitate. Dual surveys were performed next to indicate the process conditions at which where the highest amounts of $CaCO_3$ precipitate could be expected.

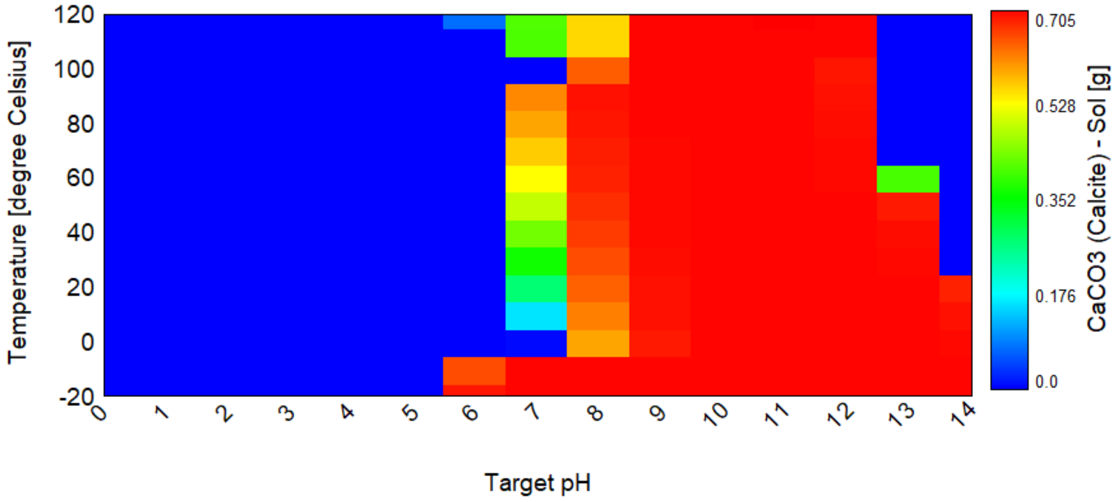

Figure 27: Variation on $CaCO_3$ precipitate subject to variation in pH and T

The simultaneous variation of pH and T (Figure 27) indicates that it is possible to precipitate the maximum amount of $CaCO_3$ over a large range of values of pH – T. The pH – P survey (Figure 28) reiterates the findings from the individual surveys i.e. the variation in pressure has no significant impact on the amount of $CaCO_3$ precipitated. The T-P survey (Figure 29) indicates that while the variation of T may have a relatively larger impact on the amount of $CaCO_3$ precipitated compared to the variation of P, the difference in amount of $CaCO_3$ precipitated is not that large.

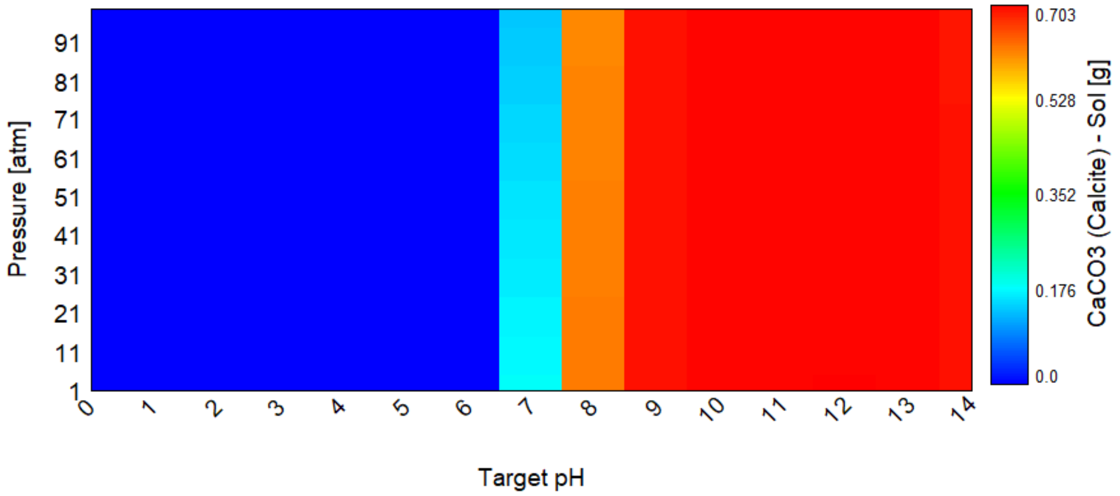

Figure 28: Variation on $CaCO_3$ precipitate subject to variation in pH and P

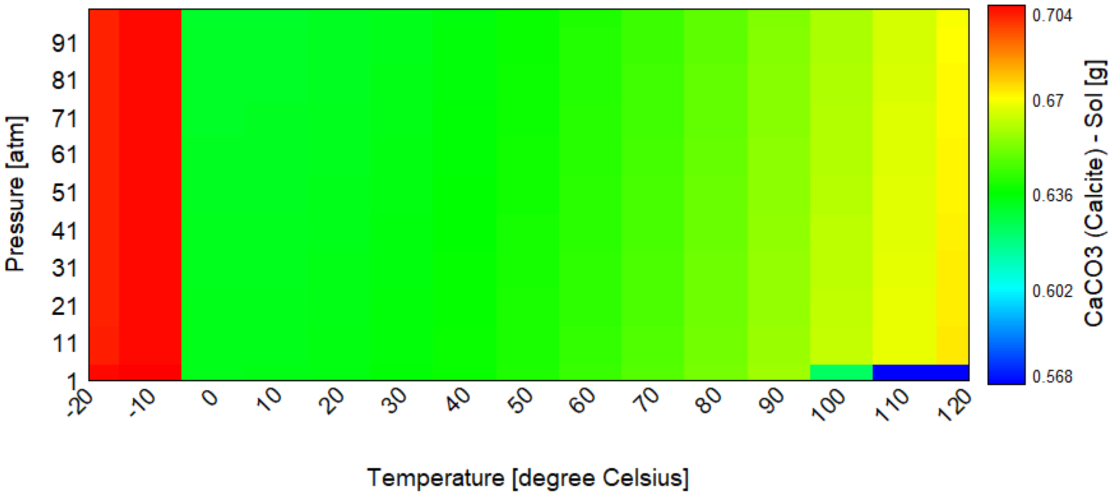

Figure 29: Variation on $CaCO_3$ precipitate subject to variation in T and P

Overall, it can be observed that pH is the most important process condition to determine the amount of $CaCO_3$ precipitating. T plays a minor role while P plays no role. The manipulation of T could result in a higher amount of $CaCO_3$ being precipitated. However, it is likely that the increase in $CaCO_3$ precipitated (just due to variation of T) would be impractical compared to the amount of energy required to vary the T. Therefore, to identify the most suitable conditions for precipitating $CaCO_3$, only pH was considered as a variable to be adjusted while T and P were kept constant at their original values (i.e. 11.5 °C and 1 atm). A pH survey was run again in higher detail (smaller step size) and the data point were analysed. The process conditions that fit the three chosen criteria the best is indicated in Table 12.

Table 12: Process conditions satisfying the selection criteria for $CaCO_3$ precipitation and their corresponding outputs.

	Units	**Best outcome**		
		Criteria A	Criteria B	Criteria C
Process Conditions				
pH	-	8.7	11.6	8.1
T	°C	11.5	11.5	11.5
P	atm	1	1	1
Precipitates formed				
$CaCO_3$	g/L	0.684	0.703	0.636
$Mg(OH)_2$	g/L	0	0.159	0
$SrCO_3$	g/L	0	0.0031	0
$BaSO_4$	g/L	0.00034	0.00033	0.00034
Purity ($CaCO_3$)	%	99.951	81.251	99.947

Between the three outcomes, the one satisfying Criteria B was not considered due to its lower purity. A lower purity would mean that resources that could be recovered at a later stage (such as $Mg(OH)_2$ and $SrCO_3$) would not be recovered as they were lost as impurities. While the outcomes satisfying Criteria A and Criteria C both have similar purity, Criteria A was chosen as the best overall outcome. Criteria C may use less chemicals for pH adjustment, it recovers a lower absolute amount of

$CaCO_3$. Since the overall purpose of this pre-treatment scheme was to separate Sr from the other ions as much as possible, priority was given to the outcome satisfying Criteria A.

Therefore, by adjusting the pH of the concentrate to 8.7 it is possible to obtain 0.684 g of $CaCO_3$ per litre of concentrate treated. This precipitate has a purity of 99.95% and corresponds to recovering 97.12% and 64.7% of Ca and C present originally in the concentrate.

3.3.2. Pre – treatment Step 2: Recovery of $Mg(OH)_2$

Once the process conditions to facilitate the precipitation of $CaCO_3$ were fixed, the precipitates formed were separated from the aqueous component. The aqueous component was subject to the same procedure to identify the next target for recovery. The composition of the aqueous stream post $CaCO_3$ precipitation is shown in Table13.

Table 13: Concentration of different elements in the concentrate post $CaCO_3$ precipitation

Element	Total Concentration (mg/L)
Na	532.3
Ba	0.011
Ca	8.13
Mg	67.2
Sr	1.91
C	44.9
S	95.7
N	0.92
Cl	681

A pH survey on this aqueous stream (Figure 30) indicates that through the variation in pH alone it is possible to precipitate $Mg(OH)_2$, $CaCO_3$, $SrCO_3$ and $BaSO_4$. The precipitation of $CaCO_3$ is still observed on account of the fact that not all Ca could not be recovered with the choice made (Criteria A). While these were the same precipitates being observed as in the previous pre-treatment step, the amount of $CaCO_3$ and $BaSO_4$ is considerably lower.

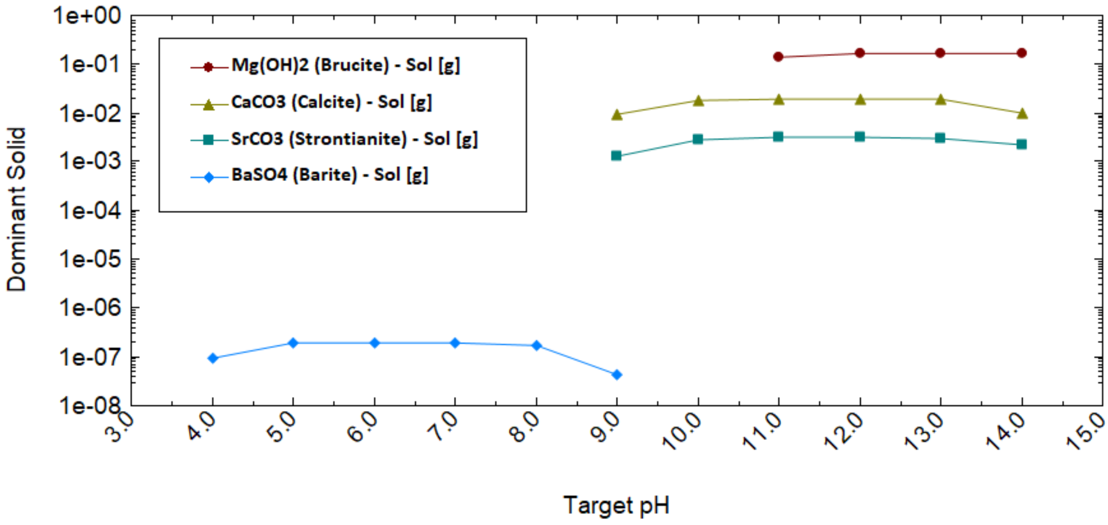

Figure 30: Precipitates formed in concentrate (post $CaCO_3$ precipitation) subject to different pH value

The individual variation of T (Figure 31) and P (Figure 32) at the given pH (8.7) do not indicate any considerable precipitation. $CaCO_3$ and $BaSO_4$ are precipitating as the pH is still favourable for the same. However, towards a higher temperature, a certain degree of $Mg(OH)_2$ precipitation was observable.

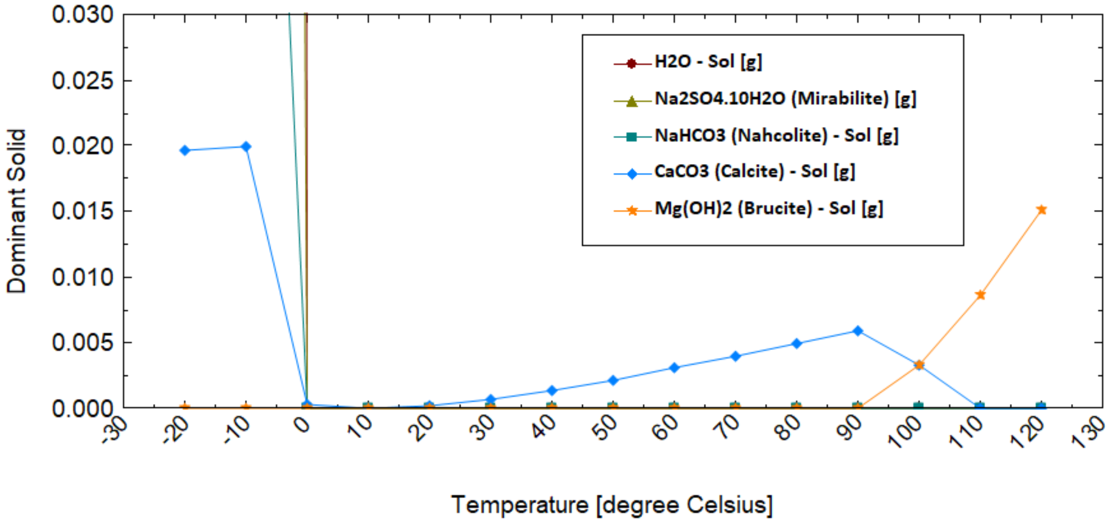

Figure 31: Precipitates formed in concentrate (post $CaCO_3$ precipitation) subject to different T value

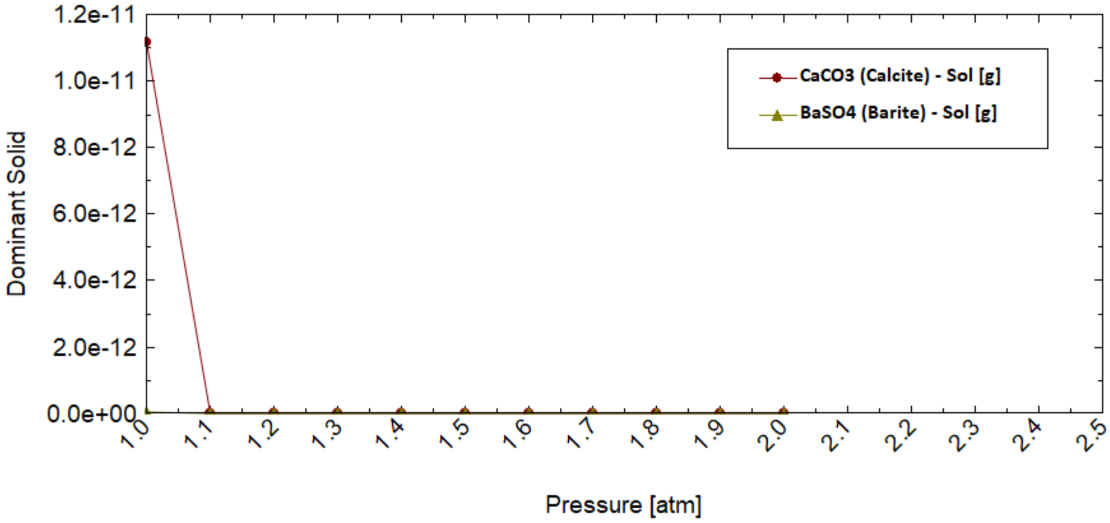

Figure 32: Precipitates formed in concentrate (post $CaCO_3$ precipitation) subject to different P value

From the individual surveys it is evident that at the given process conditions there is no main precipitate. However, if the pH was to be increased, $Mg(OH)_2$ precipitation could be observed in a reasonable (and relatively highest) quantity. Therefore, for this pre-treatment step, $Mg(OH)_2$ was targeted as the main precipitate while the rest of the precipitating components would be considered as impurities.

Next, the dual surveys were undertaken to explore the most suitable conditions to facilitate $Mg(OH)_2$ recovery via precipitation. The pH – T simulation (Figure 33) indicates that a high pH and high T are beneficial to maximize the amount of $Mg(OH)_2$ precipitated.

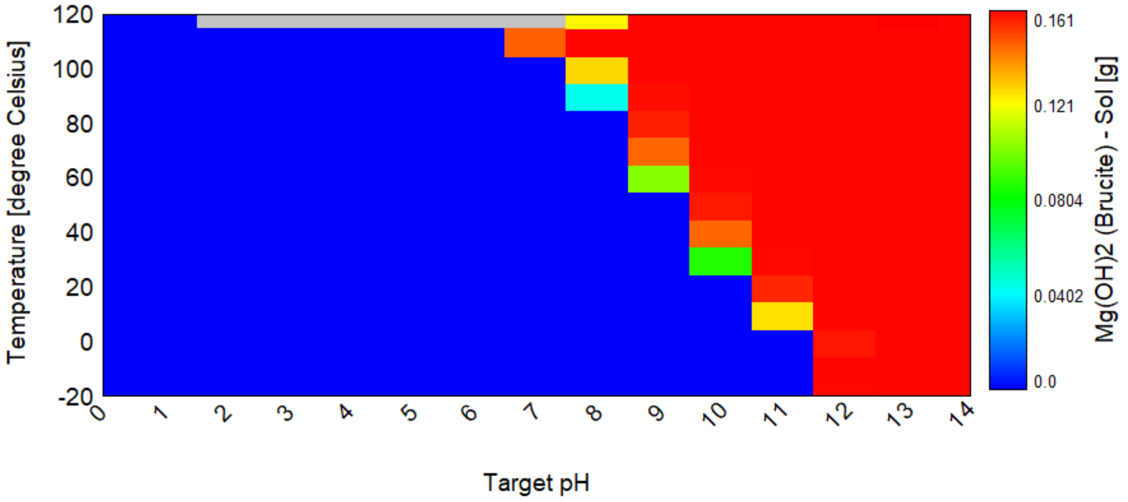

Figure 33: Variation on $Mg(OH)_2$ *precipitate subject to variation in pH and T*[11]

The pH – P simulation (Figure 34) did not reveal any new information. The T-P survey (Figure 35) confirmed that a high temperature was required to maximise the $Mg(OH)_2$ precipitated. However, the positive effect of a high T was negated at higher P values

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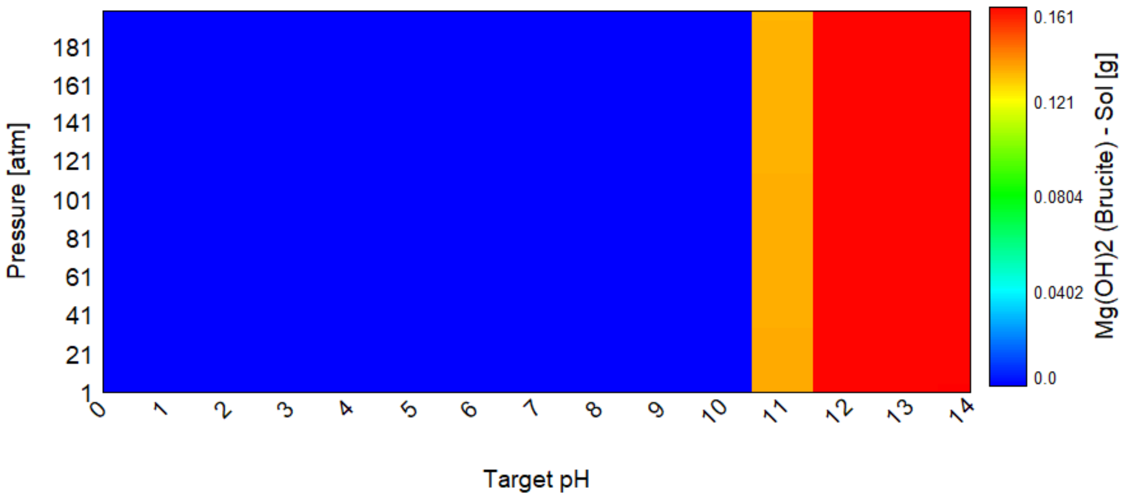

Figure 34: Variation on $Mg(OH)_2$ *precipitate subject to variation in pH and P*

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[11] Grey zones in graphs indicate combinations of variables at which simulations couldn't be carried out

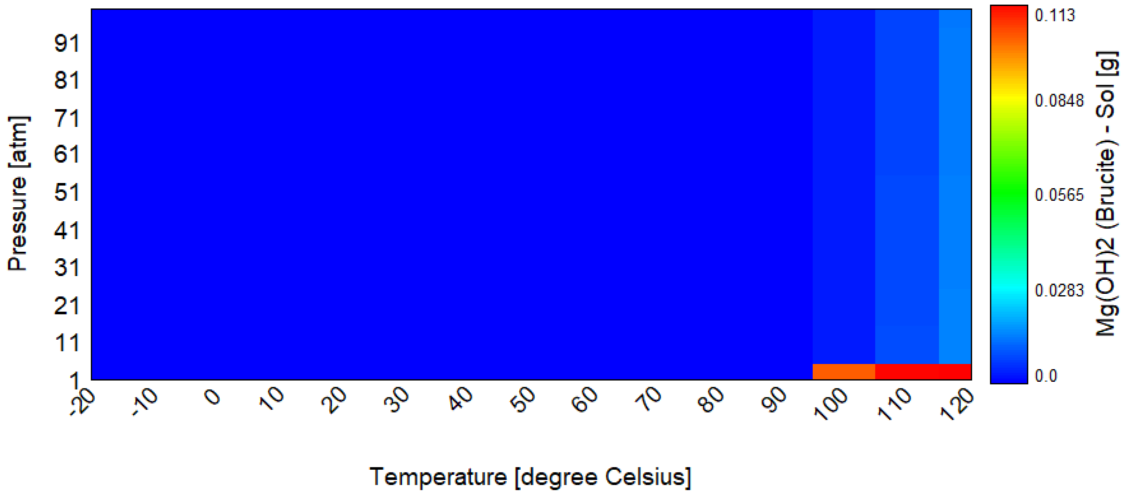

Figure 35: Variation on $Mg(OH)_2$ precipitate subject to variation in T and P

A more detailed pH – T survey was simulated to identify the most suitable outcomes. This detailed simulation was run at a P of 1.4 atm[12] (saturation pressure) to prevent the entire stream from evaporating at the final equilibrium conditions. The process conditions that fit the three chosen criteria the best is indicated in Table 14.

Table 14: Process conditions satisfying the selection criteria for $Mg(OH)_2$ precipitation and their corresponding outputs

	Units	**Best outcome**		
		Criteria A	Criteria B	Criteria C
Process Conditions				
pH	-	7.9	12	12
T	°C	100	100	70
P	atm	1.4	1.4	1.4
Precipitates formed				
$Mg(OH)_2$	g	0.107	0.161	0.161
$CaCO_3$	g	0	0.0068	0.016
$SrCO_3$	g	0	0.0006	0.003
$BaSO_4$	g	0	0	0
Purity ($Mg(OH)_2$)	%	100	96	90

Out of the three alternatives, the one that fit Criteria B the best was chosen as the best overall outcome. Even though the process conditions for Criteria A lead to a precipitate of 100% purity, its absolute amount is considerably less than those of the other two alternatives. The process conditions for Criteria B and Criteria C offer the same amount of precipitate being formed but differ in its purity. To make an objective decision, the trade - off between Criteria B and Criteria C must be evaluated on the basis of benefits obtained by increasing the purity by 6% versus the costs of increasing the temperature by 30 °C. However, for this pre-treatment scheme Criteria B was given the preference over Criteria C as it led to lower losses of Sr in the aqueous stream as impurities with $Mg(OH)_2$ precipitate.

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[12] This value was obtained by first performing the simulation at a pressure of 1 atm. Following this the aqueous and vapour streams were subject to a pressure survey which would indicate the value of saturation pressure.

Therefore, post the recovery of $CaCO_3$, by adjusting the pH of the concentrate to 12 and temperature to 100 °C it is possible to obtain 0.161 g of $Mg(OH)_2$ per litre of concentrate treated. This precipitate has a purity of 96% and corresponds to recovering 99.99% of Mg present originally in the concentrate.

3.3.3. Pre – treatment Step 3: Recovery of $Ca(OH)_2$

Based on the chosen process conditions, $Mg(OH)_2$ precipitation was carried out. The precipitate formed was separated from the aqueous stream. The concentration of various elements in the concentrate stream subject to the chosen $CaCO_3$ and $Mg(OH)_2$ precipitation can be seen in Table 15. The increase in the total concentration of Na can be attributed to the use of NaOH for increasing the pH during the recovery of $Mg(OH)_2$.

Table 15: Concentration of different elements in the concentrate post $CaCO_3$ and $Mg(OH)_2$ precipitation

Element	Total Concentration (mg/L)
Na	17860
Ba	0.01
Ca	4.25
Mg	3.2×10^{-5}
Sr	1.21
C	34.47
S	75
N	0.72
Cl	533

A pH survey (Figure 36) on this aqueous stream indicates that while $SrCO_3$ is precipitating, further pre-treatment is needed to remove the residual Ca. Recovering Sr as $SrCO_3$ at this stage will lead to a low purity as $CaCO_3$ is expected to precipitate over the exact same range as $SrCO_3$ and in a relatively larger quantity.

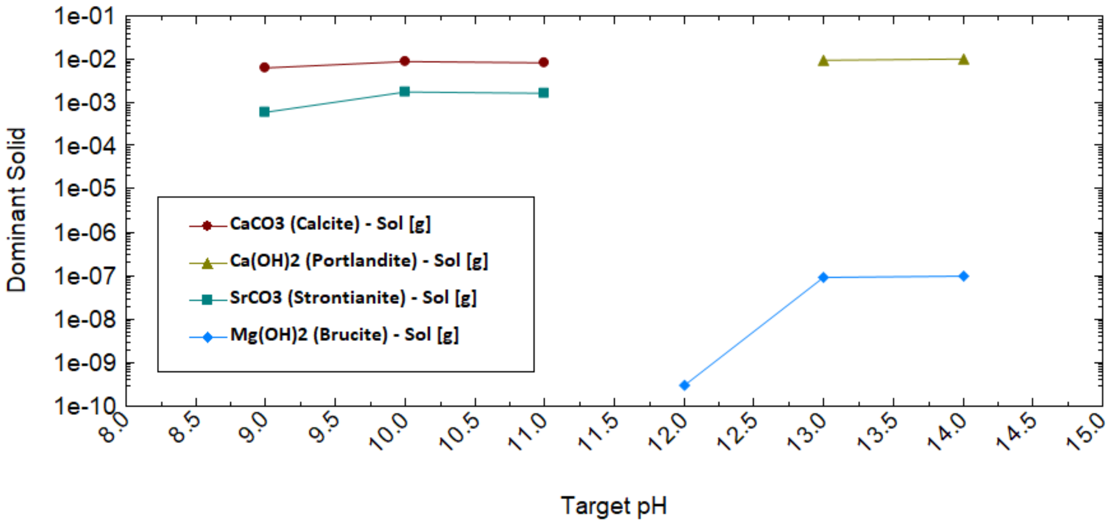

Figure 36: Precipitates formed in concentrate (post $CaCO_3$ and $Mg(OH)_2$ precipitation) subject to different pH value

From the T survey (Figure 37) it can be seen that by increasing the temperature to >100 °C it is possible to increase the amount of $SrCO_3$ precipitating in comparison to $CaCO_3$. However, at higher temperatures, the precipitation of $Ca(OH)_2$ is observed. This $Ca(OH)_2$ precipitation is larger in quantity than the $SrCO_3$ precipitated.

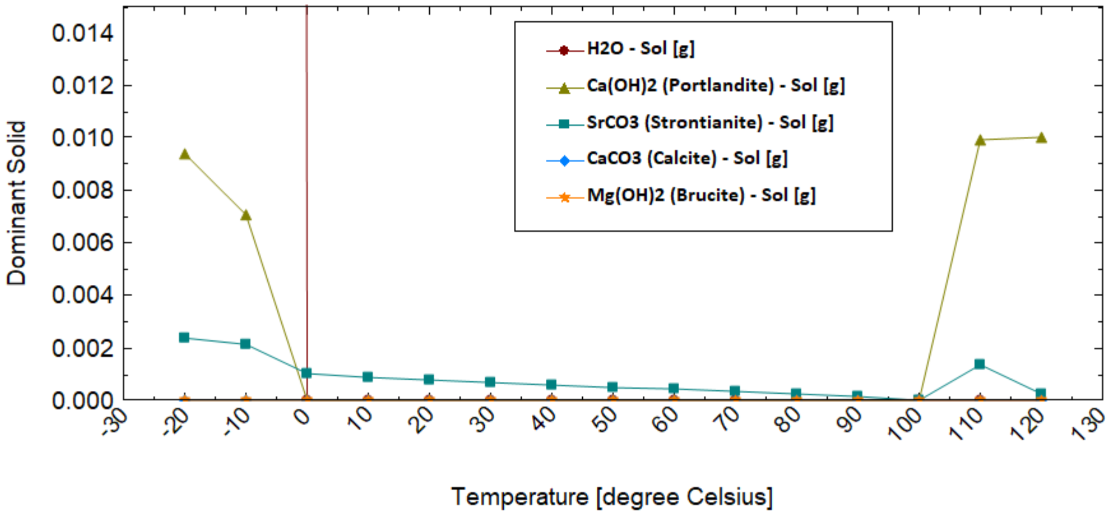

Figure 37: Precipitates formed in concentrate (post $CaCO_3$ and $Mg(OH)_2$ precipitation) subject to different T value

A P survey (Figure 38) indicated that even a slight increase in pressure results in all the precipitates dissolving back in the solution. Therefore, increasing the pressure would be detrimental to the precipitation of $CaCO_3$ and $SrCO_3$.

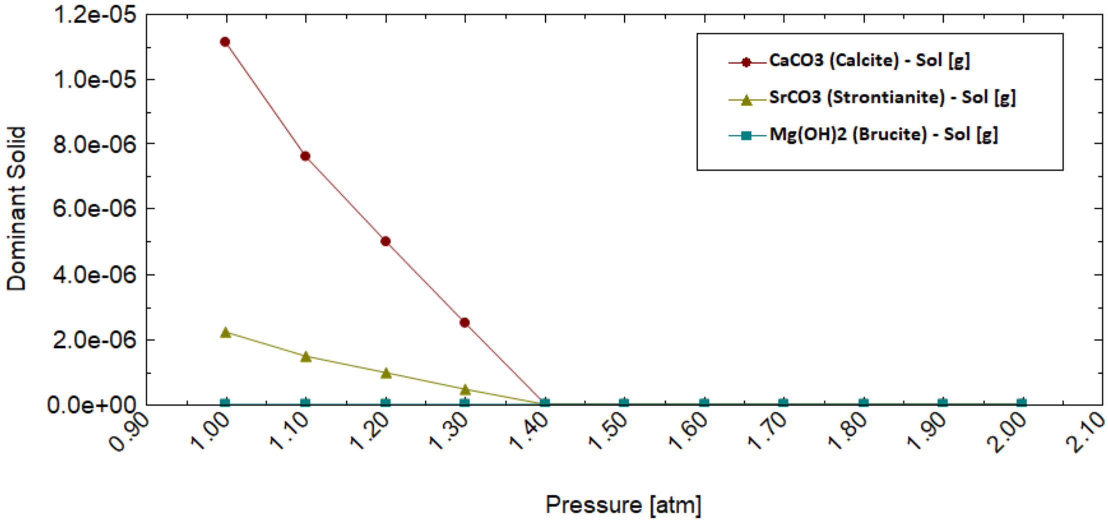

Figure 38: Precipitates formed in concentrate (post $CaCO_3$ and $Mg(OH)_2$ precipitation) subject to different P value

To be able to recover Sr as $SrCO_3$ it is evident that the amount of Ca needs to be reduced. However, considering that the precipitation of $CaCO_3$ is observed over the same conditions as $SrCO_3$, $CaCO_3$ precipitation cannot be used as the pre-treatment step. However, the pH – survey indicated that the precipitation of $Ca(OH)_2$ can also occur at a high pH range without the precipitation of $SrCO_3$. This would allow for the separation of Ca from Sr. Therefore, for this pre-treatment step, $Ca(OH)_2$ was considered as the main precipitate.

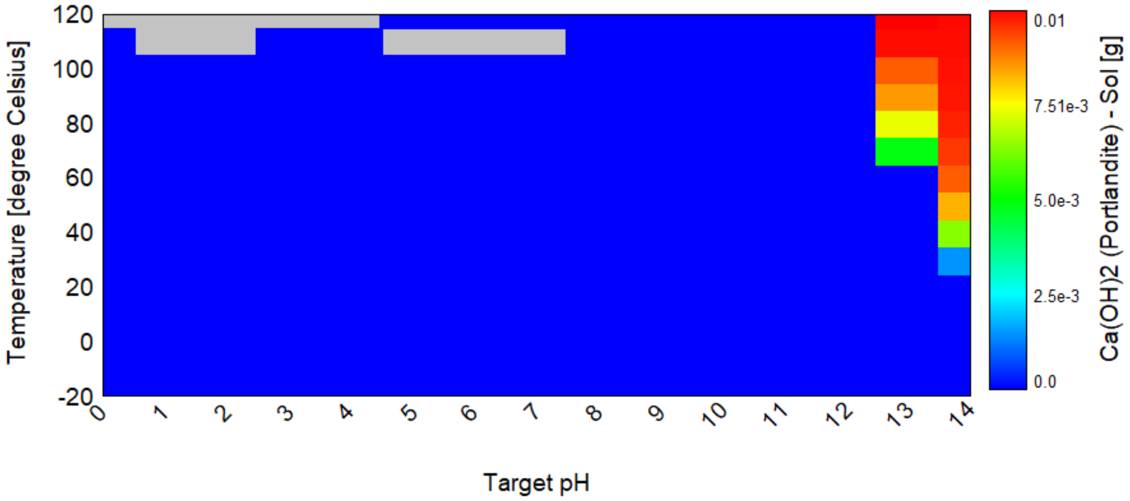

Figure 39: Variation on $Ca(OH)_2$ precipitate subject to variation in pH and T

The performed pH – T survey (Figure 39) indicates that a combination of high pH and high temperature is required to maximise the amount of $Ca(OH)_2$ precipitating. A pH – P (Figure 40) and T – P (Figure 41) survey reiterate the same point.

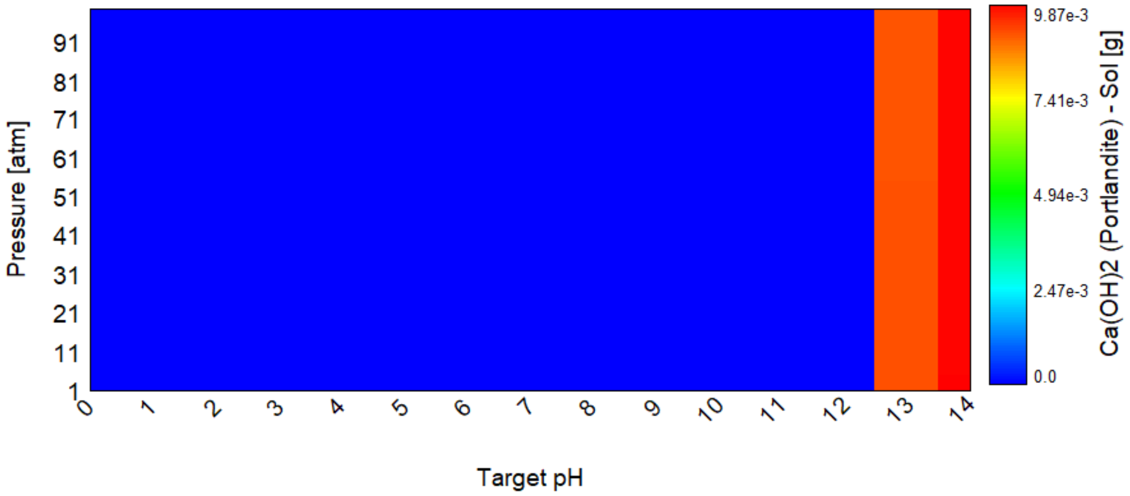

Figure 40: Variation on $Ca(OH)_2$ precipitate subject to variation in pH and P

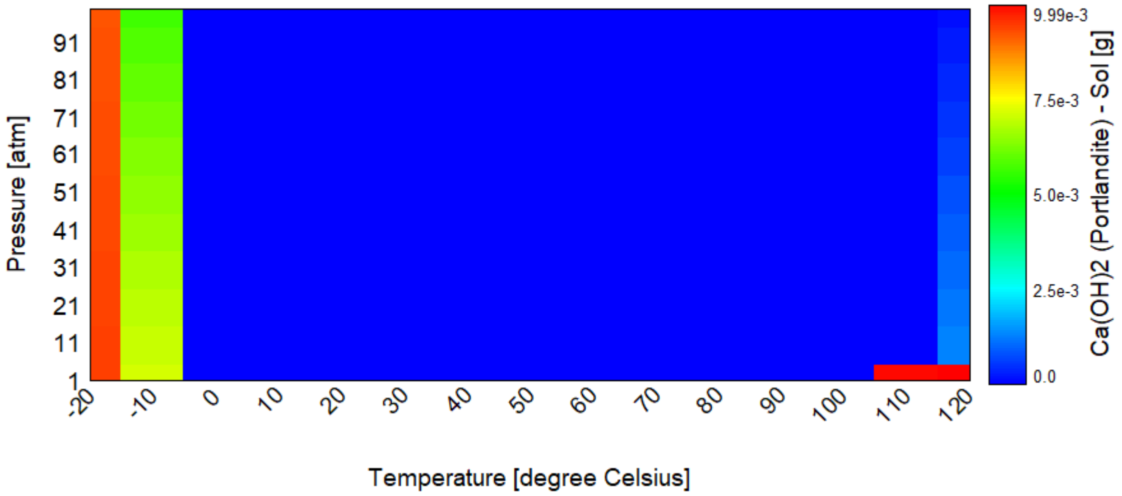

Figure 41: Variation on $Ca(OH)_2$ precipitate subject to variation in T and P

Based on the findings, a more detailed simulation was run to identify the most suitable conditions for precipitating $Ca(OH)_2$. Table 16 shows the outcomes that best fit the pre-defined criteria for selection. The same outcome satisfies both Criteria A and C. The alternative for Criteria B is able to recover a larger amount of Ca in absolute amount, the relative increase in comparison the alternative is not substantial especially in comparison to the energy required to maintain the higher temperature. Therefore, the alternative satisfying both Criteria A and Criteria C was chosen as the best set of process conditions to precipitate $Ca(OH)_2$ in this pre-treatment stage.

Table 16: Process conditions satisfying the selection criteria for $Ca(OH)_2$ precipitation and their corresponding outputs

	Units	**Best outcome**		
		Criteria A	Criteria B	Criteria C
Process Conditions				
pH	-	14	14	14
T	°C	50	100	50
P	atm	1	1	1
Precipitates formed				
$Mg(OH)_2$	g	7.89E-08	9.87E-08	7.89E-08
$CaCO_3$	g	0	0	0
$SrCO_3$	g	0	0	0
$BaSO_4$	g	0	0	0
$Ca(OH)_2$	mg	8.265	9.987	8.265
Purity ($Ca(OH)_2$)	%	99.99	99.99	99.99

Therefore, post the recovery of $CaCO_3$ and $Mg(OH)_2$, by adjusting the pH of the concentrate to 14 and temperature to 50 °C it is possible to obtain 8.27 mg of $Ca(OH)_2$ per litre of concentrate treated. This precipitate has a purity of 99.99% and corresponds to recovering 82.4% of Ca present prior this precipitation step.

3.4. $SrCO_3$ precipitation

Table 17: Concentration of different elements in the concentrate post $CaCO_3$, $Mg(OH)_2$ and $Ca(OH)_2$ precipitation

Element	Total Concentration (mg/L)
Na	104557
Ba	0.01
Ca	0.92
Mg	8.6×10^{-6}
Sr	1.5
C	43
S	93
N	0.89
Cl	661

Through the various pre-treatment steps described most of the ions were separated from Sr. The composition of the concentrate after all the pre-treatment steps can be seen in Table 17. Based on the current composition, it should be possible to precipitate $SrCO_3$. The major cation present apart from Sr is Na which should ideally have no impact on $SrCO_3$ precipitation. The major anions present are Cl, S and C. The presence of Cl should also have no impact on the precipitation of $SrCO_3$ while the effect of S could be mitigated through variation of pH. The procedure used to identify the pre-treatment steps was implemented to identify the most suitable process conditions for the precipitation of $SrCO_3$.

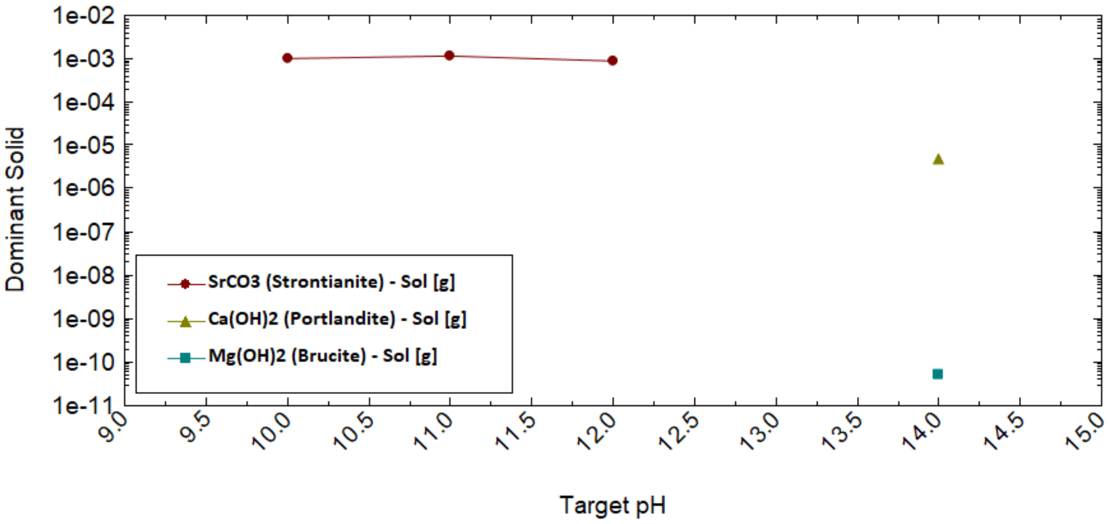

Figure 42: Precipitates formed in concentrate (post $CaCO_3$, $Mg(OH)_2$ and $Ca(OH)_2$ precipitation) subject to different pH value

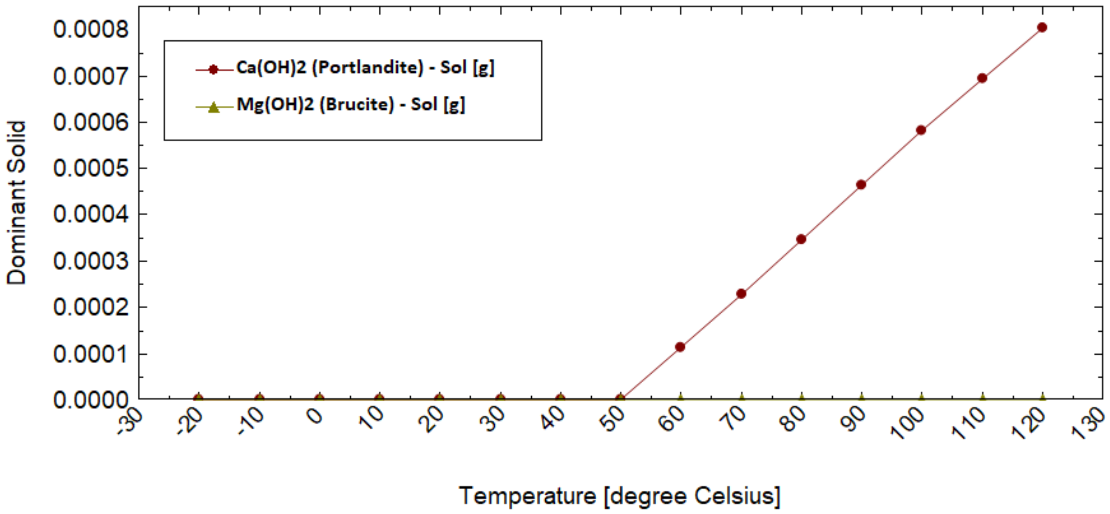

Figure 43: Precipitates formed in concentrate (post $CaCO_3$, $Mg(OH)_2$ and $Ca(OH)_2$ precipitation) subject to different T value

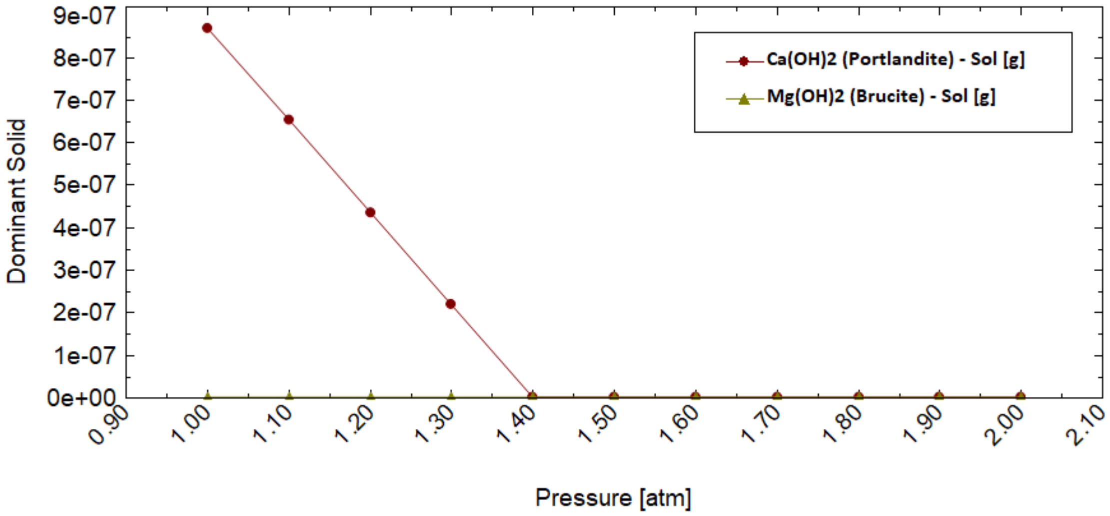

Figure 44: Precipitates formed in concentrate (post $CaCO_3$, $Mg(OH)_2$ and $Ca(OH)_2$ precipitation) subject to different P value

The output from the six simulation can be seen in Figures 42 - 47. The surveys indicate that $SrCO_3$ precipitation is observable in a specific pH range (9.5 – 12.5) and is favoured by a high temperature. The individual survey of pressure and T – P survey do not add any information for $SrCO_3$ precipitation as the pH for the same is not suitable. From the pH – P dual survey it is indicated that increasing the P may lead to reduction in the amount of $SrCO_3$ precipitated and it would be preferable to not increase it.

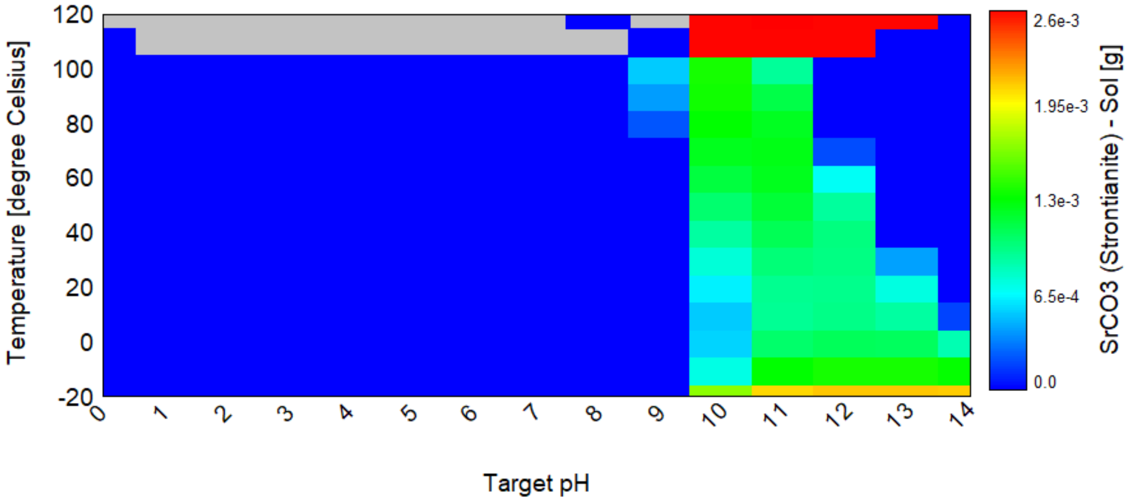

Figure 45: Variation on $SrCO_3$ precipitate subject to variation in pH and T

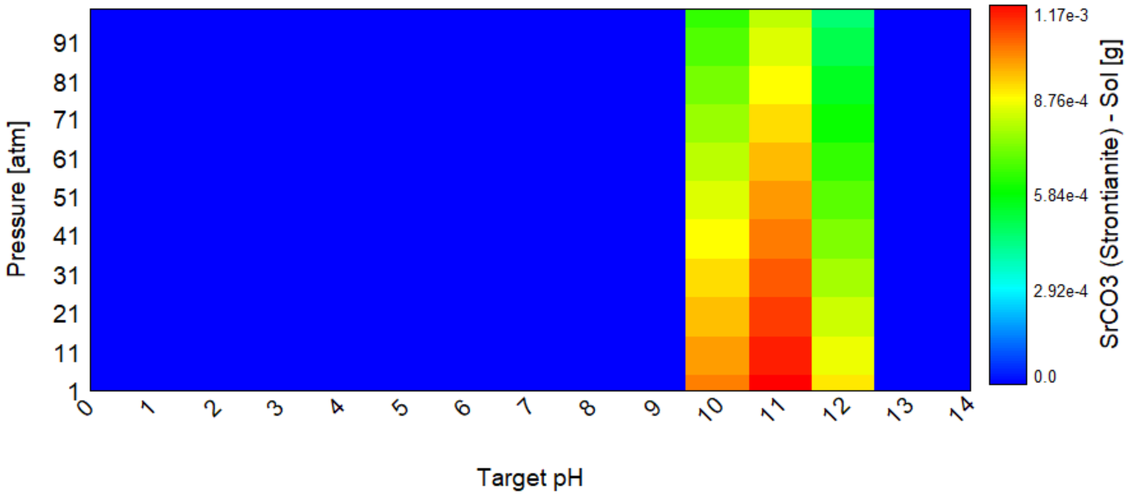

Figure 46: Variation on $SrCO_3$ precipitate subject to variation in pH and P

Based on the obtained information, a more detailed simulation was carried out. Based on the data from the detailed simulation, the most suitable process conditions for the precipitation of $SrCO_3$ are shown in Table 18. Since no other precipitate was being formed under these conditions, the purity of $SrCO_3$ in all cases was 100%, i.e. all outcomes satisfied Criteria A. The alternative satisfying Criteria B allows for the precipitation of a larger $SrCO_3$ amount but at the expense of higher temperature and use of more chemicals.

Therefore, through the above simulations it can be seen that the recovery of $SrCO_3$ is technically feasible from concentrate created during drinking water production. The recovery is based only on the variation of process conditions of pH, T and P and is subject to certain pre-treatment step. 0.0014 g of $SrCO_3$ at 100% purity can be recovered per litre of concentrate. This corresponds to a recovery of 60.16% of the total Sr present in the concentrate originally. The elemental composition of the concentrate post $SrCO_3$ precipitation is presented in Table 19.

Table 18: Process conditions satisfying the selection criteria for $SrCO_3$ precipitation and their corresponding outputs

	Units	Best outcome		
		Criteria A	Criteria B	Criteria C
Process Conditions				
pH	-	-	10.2	11.3
T	°C	-	90	30
P	atm	-	1	1
Precipitates formed				
$Mg(OH)_2$	g	-	0	0
$CaCO_3$	g	-	0	0
$SrCO_3$	mg	-	1.372	1.009
$BaSO_4$	g	-	0	0
$Ca(OH)_2$	g	-	0	0
Purity ($SrCO_3$)	%	-	100	100

Table 19: Concentration of different elements in the concentrate post $CaCO_3$, $Mg(OH)_2$, $Ca(OH)_2$ and $SrCO_3$ precipitation

Element	Total Concentration (mg/L)
Na	88166
Ba	0.01
Ca	0.77
Mg	7.2×10^{-6}
Sr	0.6
C	36
S	78
N	0.75
Cl	135295

Post the precipitation of $SrCO_3$, the remaining concentrate represents a NaCl solution of 4.65M strength. This NaCl solution reached such a high concentration primarily due to addition of sodium hydroxide (NaOH) and hydrochloric acid (HCl) for adjustment of pH. This solution has a high purity and could be considered for purposes such regeneration of ion exchange columns etc. An overview of the resources recovered is presented in Table 20. The amount of precipitates recovered on an annual basis has also been calculated taking into account 8 hours a day operation for each day of the year.

Table 20: Overview of the recovered resources

Resource	Recovered amount	Purity	Recovery Rate	Annual recovered amount
	g/L concentrate			Tonnes/year
$CaCO_3$	0.684	99.95%	97.12%	1006.6
$Mg(OH)_2$	0.161	96%	99.99%	236.94
$Ca(OH)_2$	0.0083	99.99%	82.4%	12.21
$SrCO_3$	0.0014	100%	60.16%	2.06

4. Experimental Design

Chapter Summary: **Through the knowledge gained on identification of relevant factors (Chapter 2) and expected conditions in real industrial concentrate (Chapter 3), this chapter delves into the multiple facets of designing independent experiments to quantify the relationship between multiple factors and their effect on $SrCO_3$ precipitation. First, the concept of "Design of Experiments" is introduced briefly. Next, the reasons for selecting the chosen independent variables, range of study and dependent variables is elaborated upon. The table of experiments is presented. Lastly, the collections of responses are discussed.**

4.1. Design of Experiments

Design of Experiments (DOE) has been defined as "the process of planning the experiment so that appropriate data will be collected and analysed by statistical methods, resulting in valid and objective conclusions"[67]. The basic purpose of DOE is to develop a comprehensive and predictive knowledge of a complex, multivariate system/process while parallelly minimizing the number of experiments (resources, time and money) to obtain the necessary data. More specifically, through DOE, a quantifiable relationship between the dependent and independent variables is developed under the restrictions considered. DOE, developed by Ronald Fisher in 1920's is based on three basic principles:

1. Randomisation – Performing experiments in a random or arbitrary order to reduce the effect/variability of uncontrollable external factors[73] i.e. ensure that all experiments are exposed to a uniform degree of noise[74].
2. Replication – Repetition of experiments in a random sequence to decrease experimental error and thereby increase precision[75].
3. Blocking – Grouping of similar or homogenous experimental runs to variation of external noise factors and therefore increase design efficiency[75].

DOE provides an alternative to the more widely practiced One Factor At a Time (OFAT) experimental design and offers multiple advantages over it:

1. Reduced number of experiments
2. Identification of interaction effects
3. Increased precision of estimated effect[13]
4. Design Orthogonality[14]
5. Simple to achieve yet detailed statistical analysis

DOE as a concept can be applied in a variety of ways, ranging from identifying relevant factors to process optimization. Some of the standard experimental designs include screening designs, factorial designs, response surface designs, mixture designs, Taguchi designs etc[76]. Each design has a different applicability based on what is being investigated and under what practical constraints. From a research perspective, DOE has been explored for water treatment [77][78][79][80].

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[13] Effects are evaluated on the basis of averages rather than individual values allowing for a higher accuracy

[14] The effect of a variable is estimated independent of the effect of all other variables

This study uses a "Response Surface Design". This design is a used to have a more advanced understanding of a response (dependent variable) and optimize it as well. Through this design it is possible to develop a second degree mathematical model which relates the dependent variables to the independent variables. Compared to a factorial design (which is incorporated in response surface design), it allows for the estimation of quadratic terms. It is this inclusion of quadratic terms which makes it a more suitable design choice. Terms of the third order (cubic terms) or higher in general are almost never significant to the outcome while first order terms are on their own unable to encapsulate a process in its entirety. Therefore, investigation into a second degree model represents an efficient approach. Within the response surface design, it is possible to have two types of design:

(a) Central Composite Design (CCD)
(b) Box – Behnken Design (BBD)

While both alternatives can be used to estimate first and second degree terms, they have certain differences. These differences are discussed in Table 21.

Table 21: Comparison of CCD and BBD

CCD	BBD
1. Can make direct use of information obtained from a factorial design	1. Cannot make use of information obtained from a factorial design
2. Can have up to five levels per factor	2. Always have three levels per factor
3. Includes experiments with all factors at extreme setting	3. Does not include experiments with all factors at extreme setting
4. Usually contain more design points than BBD.	4. Usually contain fewer design points than CCD.

Taking into consideration that a factorial design was not used to identify relevant factors and the practical advantages of having to perform fewer experiments, a Box-Behnken type of design was given preference over the central composite design for this study.

The specifics, finer details and further explanations related to DOE are well documented and can be found in various publications[67] or even blogs[81]. Details more specific to design considerations for this study is discussed as and when required. Minitab Statistical Software[68] was used to implement DOE for this study.

4.2. Selection of Factors

"Factors" refer to the independent variables being analysed in the study. For an experimental design such as BBD, the number of factors being studied should be kept as low as possible. Based on the information available from Chapter 3 it is possible to identify the most relevant factors. If the presence and/or variation of a factor resulted in quantitative or qualitative changes on $SrCO_3$ precipitation, it would be deemed relevant.

The effect of pH, Sr, C, Ca, Ba, Mg and S on $SrCO_3$ precipitation was evident. The effect of T was observable only at low concentrations of Sr and that is why it was not considered as relevant. While Ba had an effect, it was also seen that the amount of Ba in PWN concentrate was always very low. Therefore, to reduce the number of factors studied using BBD, Ba was also not considered as a relevant factor. Thus, the factors considered for this BBD include pH, Sr, C, Ca, Mg and S.

Here, the pH is considered as the initial pH of the solution and not the process pH (maintained constant throughout the process). As will be discussed in subsequent sub-sections, experiments were performed based on the finalized experimental design. The experimental set – up did not offer the possibility to maintain a continuous pH and therefore could not be considered.

4.3. Selection of Levels

“Levels” refer to values of the factors at which they are analysed, i.e. the range of study. The upper limit of the range is referred to as high (+1) while the lower limit is referred to as low (-1). Majority of all the experiments in a design are based on combinations of these values. However, a certain set of experiments are based on the average/mean values of these ranges, also known as centre points (0). The purpose of these centre points is to identify and quantify non-linear behaviour and also check the adequacy of the mathematical model developed. Coded values (-1, 0, +1) are calculated based on actual values (uncoded values) of the factor using Eq. 7

$$\text{Coded Value} = \frac{\text{Actual Value} - \text{Mean}}{\text{High Value} - \text{Mean}} \qquad \text{Eq. (7)}$$

The levels selected for this study were based on two considerations, (i) Levels that would allow for a greater understanding of the effects of each factor and, (ii) Levels that could be expected or theoretically obtained in industrial concentrate, using PWN concentrate as an example. Based on the two considerations, the levels chosen for each factor can be seen in Table 22.

Table 22: Levels chosen for BBD

Factor	Unit	-1	0	1
pH	-	9	11	13
Sr	*mM*	0.5	0.75	1
C	*mM*	0.5	0.75	1
Ca	*mM*	0.25	1	1.75
S	*mM*	0.25	1	1.75
Mg	*mM*	0.25	1	1.75
Ba	*mM*		0.05	

For comparison, the values of the factors in the PWN concentrate including the various pre-treatment steps (Chapter 3) are provided in Table 23.

Table 23: Concentration of factors in PWN concentrate at different stages of pre-treatment

Factor	Unit	Concentrate	After Pre-treatment Step		
			1	2	3
pH	-	8.08	8.7	12	14
Sr	mM	0.022	0.022	0.014	0.017
C	mM	10.56	3.74	2.87	3.55
Ca	mM	7.04	0.203	0.106	0.023
Mg	mM	2.76	2.76	$1.35 *10^{-6}$	$3.54*10^{-7}$
S	mM	2.98	2.99	2.34	2.9
Ba	mM	$1.53*10^{-3}$	$8.28*10^{-5}$	$6.48*10^{-5}$	$8.03*10^{-5}$

An alkaline pH range was chosen as $SrCO_3$ precipitation is observed only then. In general, the range of Sr and C were kept identical as they both are driving forces the precipitation of $SrCO_3$. If they were unequal, the effect of the larger driving force could overshadow the effect of the smaller driving force and lead to incorrect conclusions. As for the competitor ions, it would be important to know how they behave when they are at a lower, equal and higher value when compared to the driving force. For the same reason, the chosen range for Ca, Mg and S was considered.

From a practical perspective, it can be confirmed that the chosen levels for pH, Ca and Mg could be at least theoretically expected in PWN concentrate. There is a considerable difference between the chosen levels of Sr, C and S and what was observable in the PWN concentrate. The levels of Sr selected was higher than the levels observed in PWN concentrate and the chosen levels of C and S were lower than what was observed in the PWN concentrate. However, certain arguments can be made that could reduce the differences between the levels considered and the levels observed in the PWN concentrate.

The levels of C and S are high in the PWN Concentrate due to the fact that only variation of process conditions was considered for pre-treatment. Theoretically, by addition of calcium chloride ($CaCl_2$) to the concentrate during the pre-treatment step 1, more $CaCO_3$ can be precipitated, resulting in lower C values. As for S, implementation of an anion exchange column could allow for reducing the levels of S while simultaneously being able to recover it as sodium sulphate (Na_2SO_4). This was not investigated and needs to be verified. The hypothesized and modified pre-treatment scheme is presented in Figure 48.

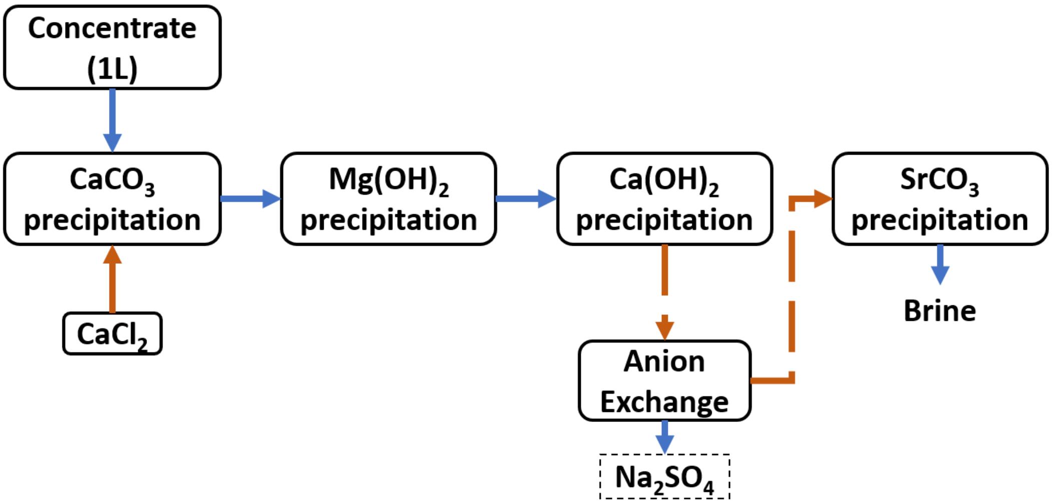

Figure 47: Pre-treatment scheme with additional proposed steps

Post the pre-treatment steps, the highest Sr concentration that could be obtained was 0.017 mM. Theoretically, a higher value can be obtained if evaporation were to be employed at this stage. Simulating this with OLI shows that subjecting the concentrate, post the precipitation of $Ca(OH)_2$, to 266 °C allows for the maximum Sr concentration of 0.138 mM, still considerably less than the chosen levels. Ideally, a higher concentration should have been reached via evaporation, but this was no possible due to the high Na and S content in the concentrate at that stage. Attempts were made to simulate nanofiltration (using IMSDesign) to separate Na from the stream. However, this could not be simulated due to different approach to charge balance in OLI and IMSDesign software's[15]. The stream

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[15] High Na in OLI output is due to addition of NaOH for pH adjustment. The charge for this is balanced by OH^- ions. However, there is no option in IMSDesign to add OH- ions. Therefore, charge balance in IMSDesign has to be carried out with Cl^- which leads to a highly saline solution.

was too saline for IMSDesign to simulate. From a different perspective, the primary reason for a low Sr concentration in the PWN concentrate is the low Sr concentration in the feed. Based on Table 2, it can be seen that relative to PWN concentrate, other streams/concentrate have a higher Sr concentration. Therefore, theoretically subject to pre-treatment (on similar line to that of PWN concentrate), it should be possible to obtain the chosen levels for Sr.

While Ba was not considered as a factor to be studied with BBD, it was considered as a factor to be kept at a constant value. Ba was shown to have impact on $SrCO_3$ precipitation both qualitatively and quantitively. However, due to its considerably low value in PWN concentrate coupled with the need to minimize the number of factors for BBD, it could not be considered. The presence of Ba could also have an indirect impact on $SrCO_3$ precipitation due to its tendency to precipitate as $BaSO_4$. The formation of BaSO4 could have a negative impact on the purity of $SrCO_3$ precipitated but at the same time potentially reduce the amount of S in the solution thereby allowing for more Sr to precipitate as $SrCO_3$. Therefore, to make the findings of BBD more representative of conditions in the concentrate, a fixed value of Ba as considered. This fixed value was 0.05 mM, 1/10th of the lower level chosen for Sr (0.5 mM). The ratio was fixed as 1/10th as this was the ratio of Ba/Sr observed in the original concentrate.

4.4. Selection of Responses

"Response" refers to the dependent variable being analysed. The primary focus of this study is to develop a deeper understanding of $SrCO_3$ precipitation. Therefore, the selected response/s should be able to characterize $SrCO_3$ precipitation both, quantitively and qualitatively. Since it is not possible to capture the required information with a single response, two individual responses were considered. The percentage amount of Sr precipitated (denoted by %Sr precipitated, Eq. 8) was used to study $SrCO_3$ precipitated quantitively while the purity of the precipitated $SrCO_3$ (denoted by $SrCO_3$ purity (%), Eq. 9) was used to study the qualitative aspect of $SrCO_3$ precipitation.

$$\%\ \mathrm{Sr\ precipitated} = \frac{\mathrm{Total\ amount\ of\ Sr\ salts\ formed\ (mmol)}}{\mathrm{Initial\ amount\ of\ Sr\ in\ solution\ (mmol)}} \times 100 \qquad \text{Eq. (8)}$$

$$\%\ \mathrm{purity\ SrCO_3} = \frac{\mathrm{Amount\ of\ SrCO_3\ precipitated\ (mmol)}}{\mathrm{Total\ amount\ of\ salts\ precipitated\ (mmol)}} \times 100 \qquad \text{Eq. (9)}$$

4.5. Final Experimental Design

The final experimental design based on the selected factors and levels is presented in Table 24. This experimental design is presented in coded form (+1, -1, 0). The actual values (uncoded form) can be seen in Table22.

4.6. Collection of Responses

4.6.1. Measurements of Interest

Equation 8 and 9 are used to calculate the responses of interest. It can be seen that the responses chosen are not measurable directly but are instead calculated based on other output variables. The variables required to calculate the responses are the amounts of different precipitates being formed. Therefore, all the salts being precipitated for the conditions defined in each individual experimental design need to be known and also quantified.

4.6.2. OLI Simulations

The responses ultimately used to analyse the outcomes were obtained by performing OLI simulation. To manipulate only the initial pH for each experimental run, three solutions of pH adjusted water were created. Each solution corresponded to the pH value of interest (9, 11 and 13) All further simulations/steps were carried out in these solutions in accordance to the required design specifications. To maintain similarity with experimental conditions, the different factors for OLI simulations were manipulated as they were to be manipulated experimentally i.e. via their chloride and sodium salts. The chemical inputs for these simulations be seen in Table 25. Values for the aqueous concentrations of individual species, total element concentration and the solids/precipitates formed was collected for every simulation. A stepwise procedure for the simulations performed can be seen in Appendix 9.4.

4.6.3. Experimental Measurements

Precipitation experiments were conducted in WaterLab, TU Delft as per the design table seen in Table 24. The primary objective of these experiments was to evaluate the difference in initial and final concentration of different ions due to the precipitation of $SrCO_3$. In the absence of a suitable analytic technique/protocol for the characterization[16] of the precipitates formed during experiments, the aqueous concentrations of different ions were used as an indicator to quantify the precipitation. If the experimentally observed changes in the aqueous concentration of different ions (due to precipitation) followed the same pattern as that predicted by OLI, it would indicate that the behaviour of the experimentally formed precipitates would also follow a similar pattern to that predicted by OLI simulations.

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[16] Identification and quantification of each individual component in a mixture of solids

Table 24: Table of experiments as per the chosen Box - Behnken Design from Minitab

Std. Order	pH	Sr	C	Ca	S	Mg
1	-1	-1	0	-1	0	0
2	1	-1	0	-1	0	0
3	-1	1	0	-1	0	0
4	1	1	0	-1	0	0
5	-1	-1	0	1	0	0
6	1	-1	0	1	0	0
7	-1	1	0	1	0	0
8	1	1	0	1	0	0
9	0	-1	-1	0	-1	0
10	0	1	-1	0	-1	0
11	0	-1	1	0	-1	0
12	0	1	1	0	-1	0
13	0	-1	-1	0	1	0
14	0	1	-1	0	1	0
15	0	-1	1	0	1	0
16	0	1	1	0	1	0
17	0	0	-1	-1	0	-1
18	0	0	1	-1	0	-1
19	0	0	-1	1	0	-1
20	0	0	1	1	0	-1
21	0	0	-1	-1	0	1
22	0	0	1	-1	0	1
23	0	0	-1	1	0	1
24	0	0	1	1	0	1
25	-1	0	0	-1	-1	0
26	1	0	0	-1	-1	0
27	-1	0	0	1	-1	0
28	1	0	0	1	-1	0
29	-1	0	0	-1	1	0
30	1	0	0	-1	1	0
31	-1	0	0	1	1	0
32	1	0	0	1	1	0
33	0	-1	0	0	-1	-1
34	0	1	0	0	-1	-1
35	0	-1	0	0	1	-1
36	0	1	0	0	1	-1
37	0	-1	0	0	-1	1
38	0	1	0	0	-1	1
39	0	-1	0	0	1	1
40	0	1	0	0	1	1
41	-1	0	-1	0	0	-1
42	1	0	-1	0	0	-1
43	-1	0	1	0	0	-1
44	1	0	1	0	0	-1
45	-1	0	-1	0	0	1
46	1	0	-1	0	0	1
47	-1	0	1	0	0	1
48	1	0	1	0	0	1
49	0	0	0	0	0	0
50	0	0	0	0	0	0
51	0	0	0	0	0	0
52	0	0	0	0	0	0
53	0	0	0	0	0	0
54	0	0	0	0	0	0

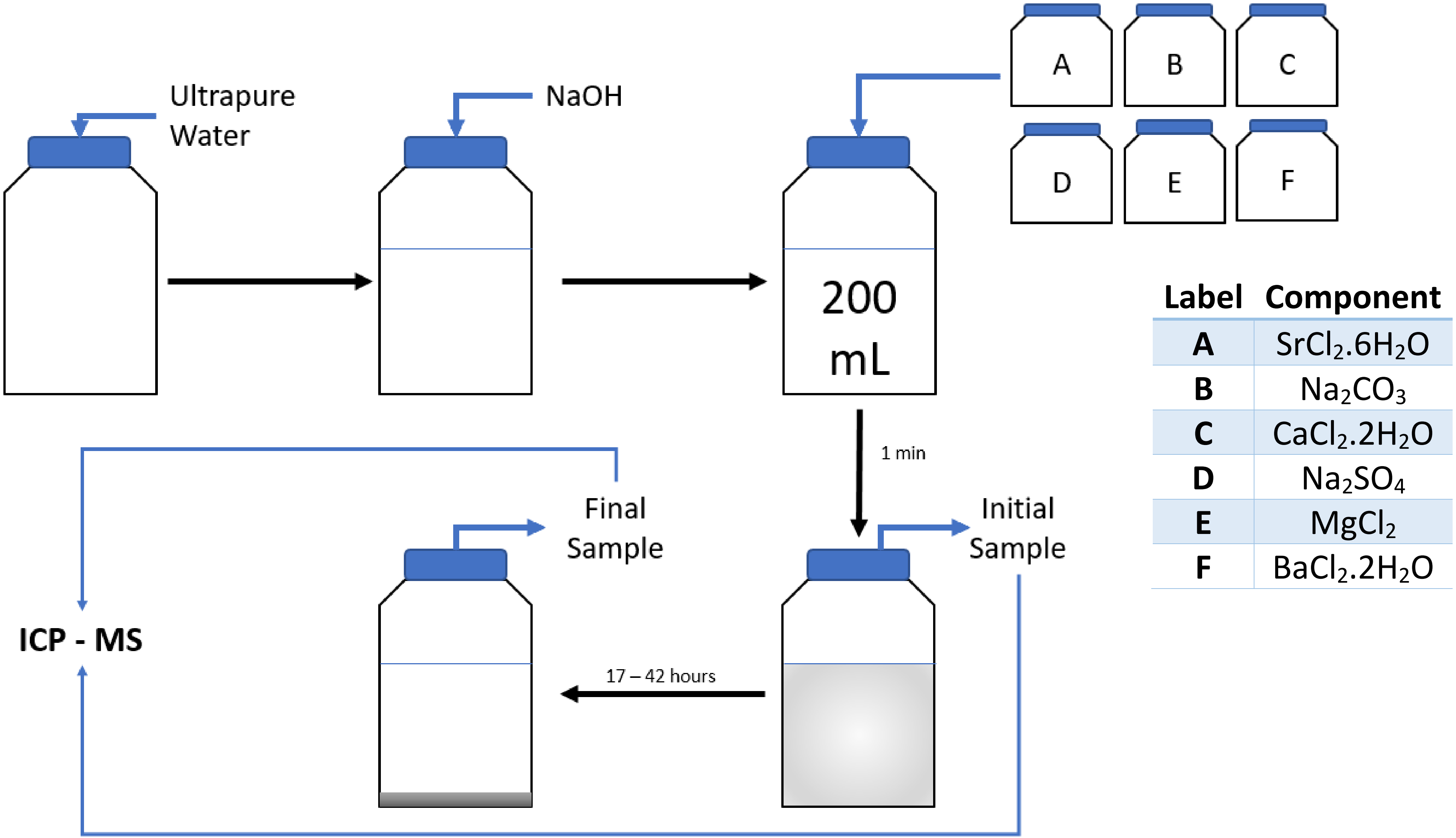
Operating Procedure

Experiments were conducted in 250 mL capped glass bottles. The initial concentration of different ions was manipulated using stock solutions. These stock solutions were prepared by dissolving the corresponding lab grade chloride salts or sodium salts of the concerned cations and anions respectively. The pH of the solution was manipulated using a NaOH solution. The stock solutions used for manipulating the levels of the facts is presented in Table 25. The chemicals used to create the stock solutions were lab grade and procured from Sigma-Aldrich.

Table 25: Solutions used to manipulate different factors

Factor	Manipulated via
pH	NaOH
Sr	$SrCl_2.6H_2O$
C	Na_2CO_3
Ca	$CaCl_2.2H_2O$
S	Na_2SO_4
Mg	$MgCl_2$
Ba	$BaCl_2.2H_2O$

To perform the experiments, the required amount of water (ultrapure) was added. The pH of the solution was then adjusted to the desired value with a NaOH solution. Subsequently, the stock solutions were pipetted in while being continuously mixed on a magnetic stirrer for uniform distribution. Experiments were performed in groups of 2, 4, or 6. Once all the stock solutions were added, the solution was mixed for a minute. For each group of experiments, a sample was collected at this stage to measure the initial concentration. The variation/deviation observed in this initial sample would be representative of the variation for that particular group of experiments and could be used as a correction factor. The solution was then left undisturbed till the time for collection of samples to measure the final concentrations. Figure 49 represents the operating procedure pictorially. Figure 50 shows a visual representation of the experimental solutions at the time of collection of initial and final samples.



Label	Component
A	$SrCl_2.6H_2O$
B	Na_2CO_3
C	$CaCl_2.2H_2O$
D	Na_2SO_4
E	$MgCl_2$
F	$BaCl_2.2H_2O$

Figure 48: Visual representation of experiments undertaken to validate results of OLI simulations used to calculate the chosen responses

The concentration of different samples was analysed through Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The ICP-MS used for this study was PlasmaQuant MS model from analytikjena.

ICP - MS was used to quantify the elements concentration of Sr, Ca, Mg, Ba and S. C could not be measured using the ICP – MS. A Total Organic Carbon (TOC) detector could also theoretically be used to measure the inorganic carbon concentration. However, owing to the mismatch between the measuring range of the equipment and the expected range of the samples, coupled with time constraints, carbon concentration was not measured in any capacity. Therefore, only the ICP – MS analysis was used to characterize the experiments and validate the OLI simulations.

Figure 49: Experimental solutions at the start of an experimental run (top) and at the end of an experimental run (bottom)

5. Experimental Validation

Chapter Summary: **This chapter compares the results obtained experimentally with the results predicted by OLI. The deviation between the two is analysed and discussion is provided explaining probable causes for the deviation.**

5.1. OLI predictions vs Experimental measurements

For the experiments to successfully validate the OLI simulations, the measured aqueous concentrations need to be in close proximity to the aqueous concentrations predicted by OLI. To confirm the similarity/dissimilarity, the data was compared in form of a ratio as seen in Equation 10 .

$$\text{Ratio} = \frac{\text{Experimentally measured concentration (mM)}}{\text{OLI predicted concentration (mM)}} \qquad \text{Eq. (10)}$$

If the experimental and predicted data were perfectly matching, the ratio would have a value of 1. A ratio > 1 would indicate that the experimental values are higher than the predicted values and a ratio < 1 would be indicative of experimental values being lower than what was predicted. The complete data set of the measured experimental concentrations and OLI predicted concentrations can be seen in Appendix 9.5. The element wise comparison for each individual experimental design can be seen in Figure 51.

From Figure 51 it can be seen that the amount of experimentally measured aqueous concentration in almost all cases in considerably higher than what is predicted by OLI. The average ratio obtained from the experiments for each element is presented in Table 26.

Table 26: Average Ratio for elements and their standard deviation

Element	n[17]	Average	Standard Deviation
Sr	51	3.58	1.86
Ca	46	3.56	4.29
Mg	42	1.84	1.33
Ba	54	59.36	61.47
S	42	7.98	10.5

Based on obtaining such a considerable difference between experimental and predicted concentrations, the OLI simulations could not be successfully validated.

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[17] The number of outliers for each element was different

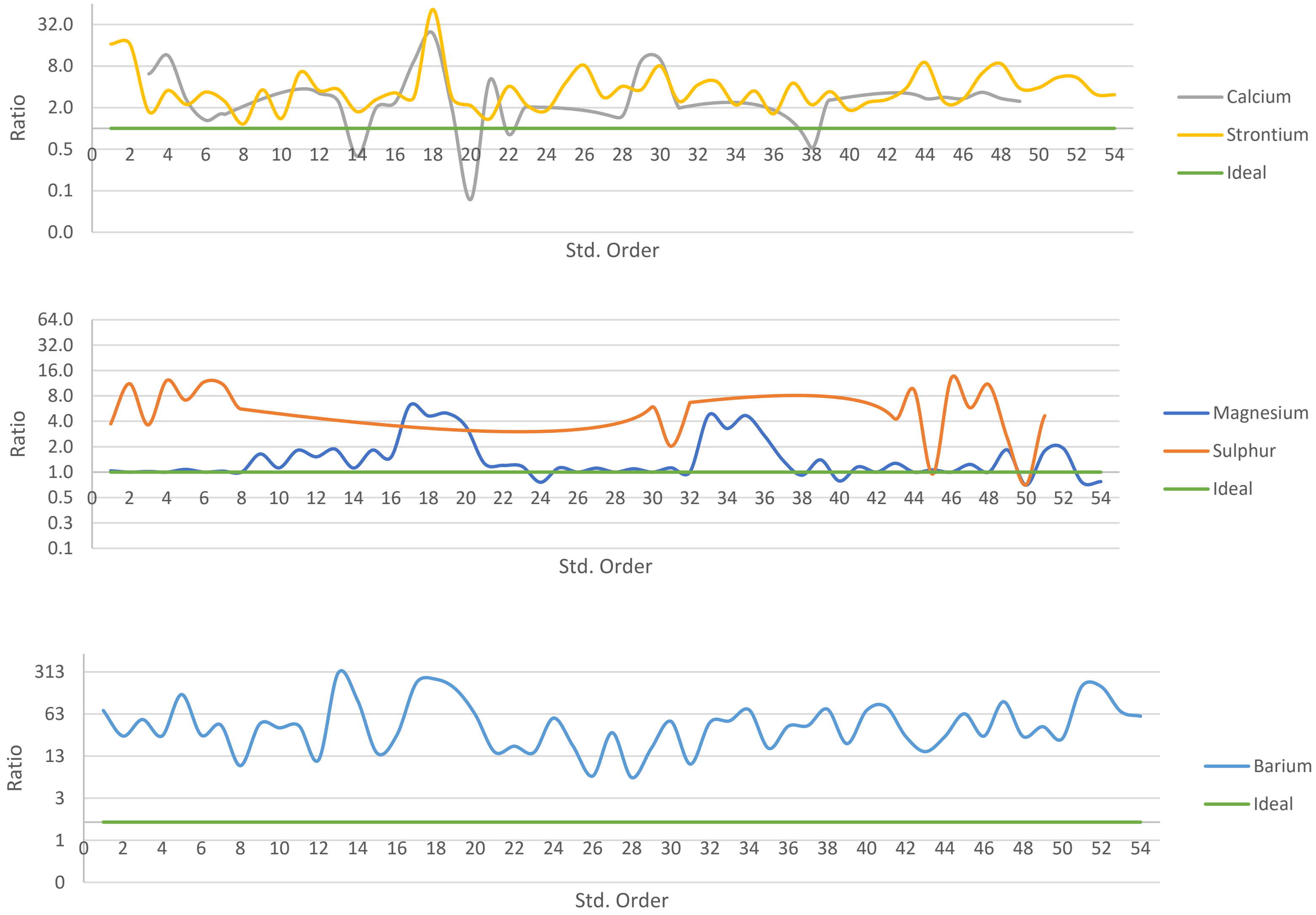

Figure 50: Ratio of experimental to OLI results for elements of Ca, Sr, Mg, S and Ba

5.2. Deviation Analysis

The presence of a considerable difference between the experimental and predicted data can be explained by either of the following two reasons:

1. Predictions made by OLI software were inaccurate
2. Experiments performed contained a faulty component

The probability of either of the possibilities occurring individually or collectively needs to be investigated in order to explain the difference in results.

5.2.1. OLI Inaccuracy

Simulations made by OLI predict the outcome based on existing knowledge and theoretical data. If a particular mechanism is not accounted for, or if there is lack of representative data, it could lead to false outcomes. Therefore, experiments are carried out to validate information obtained via simulations. Due to lack of suitable literature focussing on $SrCO_3$ precipitation using OLI, a direct analysis for the accuracy of the OLI simulations could not be made. A lack of OLI simulation - based literature for other chemical systems also prevented from indirectly verifying the accuracy of the simulations for this study. One alternative to bypass this issue would be to repeat identical simulations using the PHREEQC software and comparing the predictions from both software's[18]. Considering that substantially extensive literature is available for validating PHREEQC simulations, a similar OLI prediction could hence be validated indirectly. However, due to time constraints it was not possible to make the aforementioned comparison and remains to be carried out.

5.2.2. Experimental Error

While every consideration is taken into account to control the experiments as desired, there are bound to be certain variables that cannot be maintained and may have an impact on the final outcome. A retrospective analysis highlights certain external factors that could have had an impact on the final experimental results. An in-depth analysis also revealed that the measurements made by ICP – MS may not have been reliable enough.

External Factors

Listed below are certain factors that were not controlled/uniform during the experiments and arguments are provided to identify whether it was possible for them to have an impact.

1. CO_2 dissolution

OLI simulations are carried out in a closed system, i.e. no component is present unless specifically mentioned. This includes CO_2. However, this was not the case in the experiments performed. The experiments were carried out in 250 mL glass beakers, but the total amount of solution was only 200 mL. This meant that close to 100 mL[19] of air was also a part of the closed

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[18] In spite of both OLI and PHREEQC using theoretical information for making their predictions, a certain degree of difference between the software's prediction would be expected owing to the use of different databases and calculation frameworks.

[19] The total volume of the glass bottle was close to 300 ml

system. Since ultrapure water was used for the experiments, it meant the amount of CO_2 in the air was greater than that in the solution. This would have resulted in CO_2 dissolution to maintain equilibrium. The rate/amount of CO_2 dissolution would also vary per experimental design since each design had a different quantity of ultrapure water added and also the time taken to add the stock solutions (for which the bottle had to be opened while being mixed) was not constant. CO_2 dissolution would not only have an effect on the pH of the experiment but would also be detrimental to the precipitation of $SrCO_3$ [53]. The same situation was applicable to the various prepared stock solutions as well.

One method of eliminating this variability would be to perform experiments in glass bottles where nitrogen is bubbled into the bottle to replace the air in the set – up. This along with specific openings for addition of solutions and collection of samples should allow to minimize the amount of CO_2 exposed to the experiment and hence its effect.

2. pH variability

pH represents an important process condition hypothesized to have an impact on $SrCO_3$ precipitation. Apart from the aforementioned pH variability due to CO_2 dissolution, there could be a few more experimental conditions that could add variability to pH.

(a) Calibration of pH meter – The pH meter was calibrated each time before use using buffer solutions of 4, 7 and 10. However, the experiments were performed at pH of 9, 11 and 13. Therefore, the pH meter was used to adjust/detect pH at values higher than what it was calibrated for. It is not known if and how this could impact the accuracy of the measurement but calibrating the pH meter with a higher pH buffer (such as pH = 12) would lead to increased reliability.
(b) Variable amount of ultrapure water – Due to addition of chemical inputs through their stock solutions, ultrapure water was used to balance the rest of the volume. The initial pH of the experiment was adjusted by adjusting the pH of the added ultrapure water. Considering that each experimental design was unique, each experiment had a different amount of ultrapure water that was pH adjusted. Also considering that the pH of the stock solutions was not adjusted, there could be a significant deviation between the desired pH and the actual experimental pH due to addition of these stock solutions.
(c) Variability of adjusted pH – The pH of the solutions was adjusted to be as close to the desired value as possible. This meant that, due to human error, there were small, inconsistent deviations between the value reached and the target value. On average, the actual pH value differed from the target value by -0.03%[20]. This indicates that the deviation is very minor and is unlikely to have an impact.

To reduce the variability associated with pH, the concentration of the stock solutions can be increased or alternatively the chemicals can be added as powders. This would increase the proportion of pH adjusted water and hence reduce the variability associated with it.

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[20] The deviation ranged between -1.56% to 3.78%.

3. Time variability

   The time between starting the experiments and collecting the samples (to measure the final concentrations) ranged from 17 hours to 42 hours with an average of 31.5 hours. The time between collection of samples and measurement using ICP – MS varied anywhere from 1 hour to 21 days with an average of 7.33 days. While theoretically this time variability should not make a difference as, (i) Equilibrium (towards $SrCO_3$ precipitation) is reached and there is no external forcing to reverse it (ii) Samples during preparation are filtered, diluted, acidified and stored in a fridge. This should prevent any sizable reaction from taking place. However, it would be ideal for each sample to have the same time between sample collections and measurements to maintain uniformity[21]. Having a uniform time gap for every experimental design would reduce the scope of uncertainty.

Inadequacy of ICP - MS

Certain measurements carried out by the ICP – MS were evidently wrong. This was indicative of the fact that even if the experiments were performed perfectly, there was some unreliability associated with the measurements itself. All the measurements made by the ICP – MS were analysed from different perspectives in order to identify its reliability. Concentration of stock solutions used for experiments and initial concentrations for each experimental design were known and hence could be used to indicate the variability associated with using the ICP – MS.

It must also be considered that there is a possibility that the ICP – MS may have given faulty results due to the presence of chloride ions. Chloride ions are documented to interfere with ICP – MS analysis. These chloride ions were unavoidable due to the fact that the concentration of certain elements was manipulated via their chloride salts. Calculations carried out showed the chloride concentration for all samples to be within the acceptable limits. Thus, there was no reason to believe that high concentration of chloride ions resulted in faulty ICP – MS. However, this can only be confirmed when experiments are carried out using alternative counter ions such as nitrate.

Analysis of stock solutions

Stock solutions prepared for the experiments were analysed with the ICP-MS in multiple batches. Table 27 represent the variation between the actual and measured values for the prepared stock solutions. The complete set of data can be referred to in Appendix 9.6. The variation (%) was calculated using Equation 11.

$$\text{Variation (\%)} = \frac{\text{Measured Concentration} - \text{Actual Concentration}}{\text{Actual Concentration}} \times 100 \qquad \text{Eq. (11)}$$

Stock solutions were measured in six batches. Batch 1, 2 and 3 were individual/independent samples while Batch 4, 5, 6 can be considered as triplicates[22] taken from the same solution. The variation can be observed in Figure 52.

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[21] Due to restrictions in accessing the lab, a uniform time could not be maintained.

[22] The only difference was that the samples were collected on different days.

Table 27: Variation in stock solutions (N.D. - Not detected)

Batch	Sr	Ca	S	Mg	Ba[23]
1	7.16%	N.D.	267.02%	12.90%	2.52%
2	6.88%	-2.17%	N.D.	3.80%	<27.12%
3	6.96%	83.31%	N.D.	4.35%	<27.12%
4	5.04%	N.D.	N.D.	31.68%	-0.68%
5	0.45%	2.53%	N.D.	10.11%	<27.12%
6	-1.15%	-15.99%	N.D.	16.89%	<27.12%

Out of the five elements, only Sr and Mg were detected in all six batches. The average variation for Sr was 4.22% while the average variation for Mg was 13.29%. S was detected in only one of the six batches, and the one batch that was detected showed a variation of 267%. Ca was detected in only 4 out of the six batches with one detected sample showing an 83% variation from the expected value. As for Ba, all six batches were detected as being out of the measuring range of the equipment, however, through extrapolation the value of Ba in two out the six batches could be estimated.

Based on just the analysis of the stock solution it can be observed that there were discrepancies with measurements made with ICP – MS.

Analysis of samples for initial concentrations

Out of the 54 experiments, initial samples were collected for 15 of them. Table 28 shows the variation between the measured and expected value for the collected initial samples. The complete set of information can be found in Appendix 9.7.

Similar to what was observed with the analysis of stock solutions, S was either not detected or over detected in all samples. Ca also showed a similar trend of either not being detected (5 out of 15 samples) or immensely over detected (7 out of 15 samples). For Mg, Sr and Ba the results were more reasonable with only fewer samples showing a large variation. On average, the initial samples showed a variation of -14.85% for Sr, -21.82% for Mg and -9.37% for Ba. However, in all cases, the standard deviation associated with the variation is much larger than its average. The variations are presented graphically in Figure 53.

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[23] All six samples were above the detection/measurement range of the ICP – MS. However, through extrapolation, expected concentrations of two samples could be obtained but not for the other four. Ba concentrations for these four samples are thus presented as a range. They were not use for the calculations of average and standard deviation

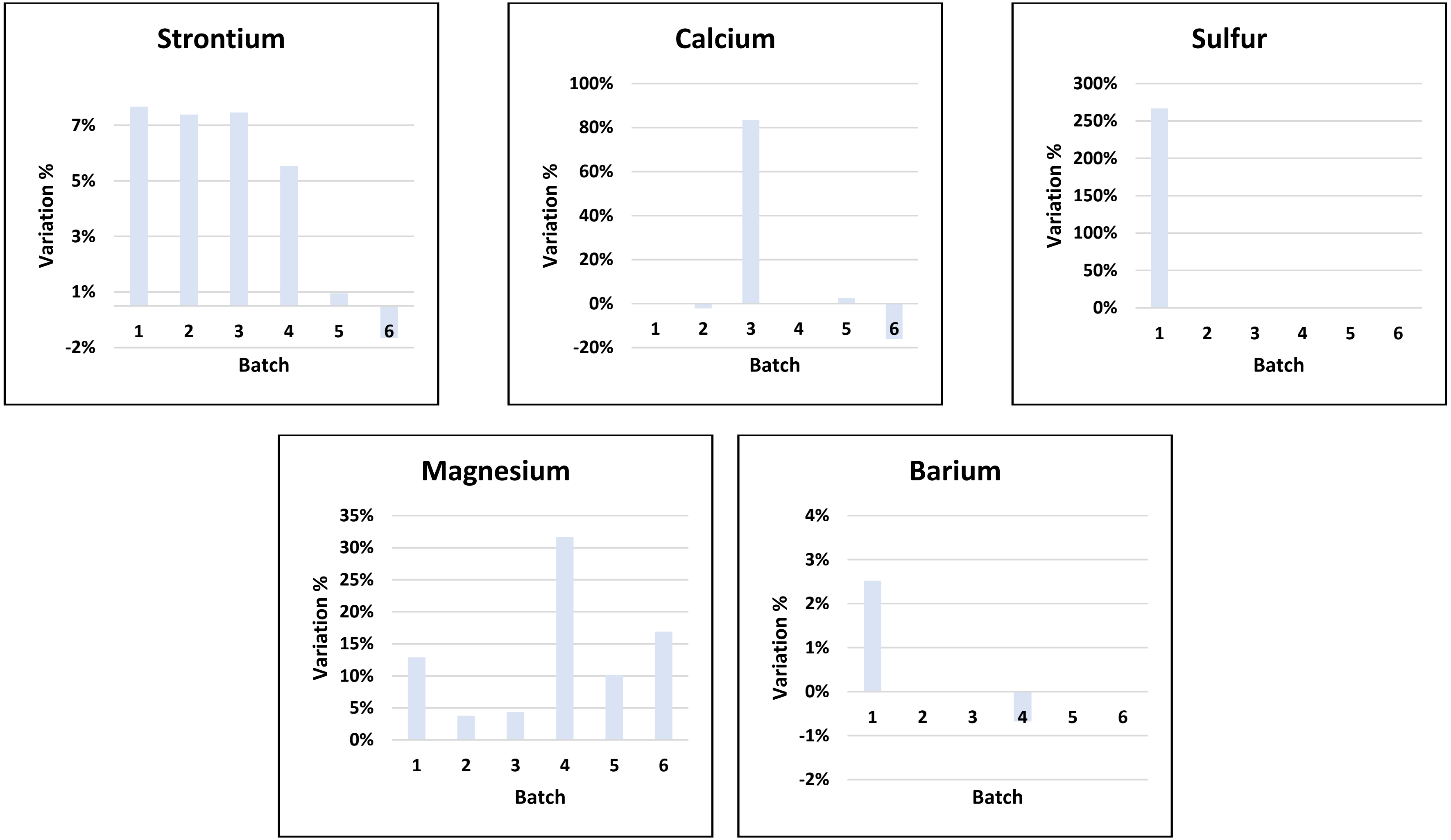

Figure 51: Observed variation amongst elements in stock solutions

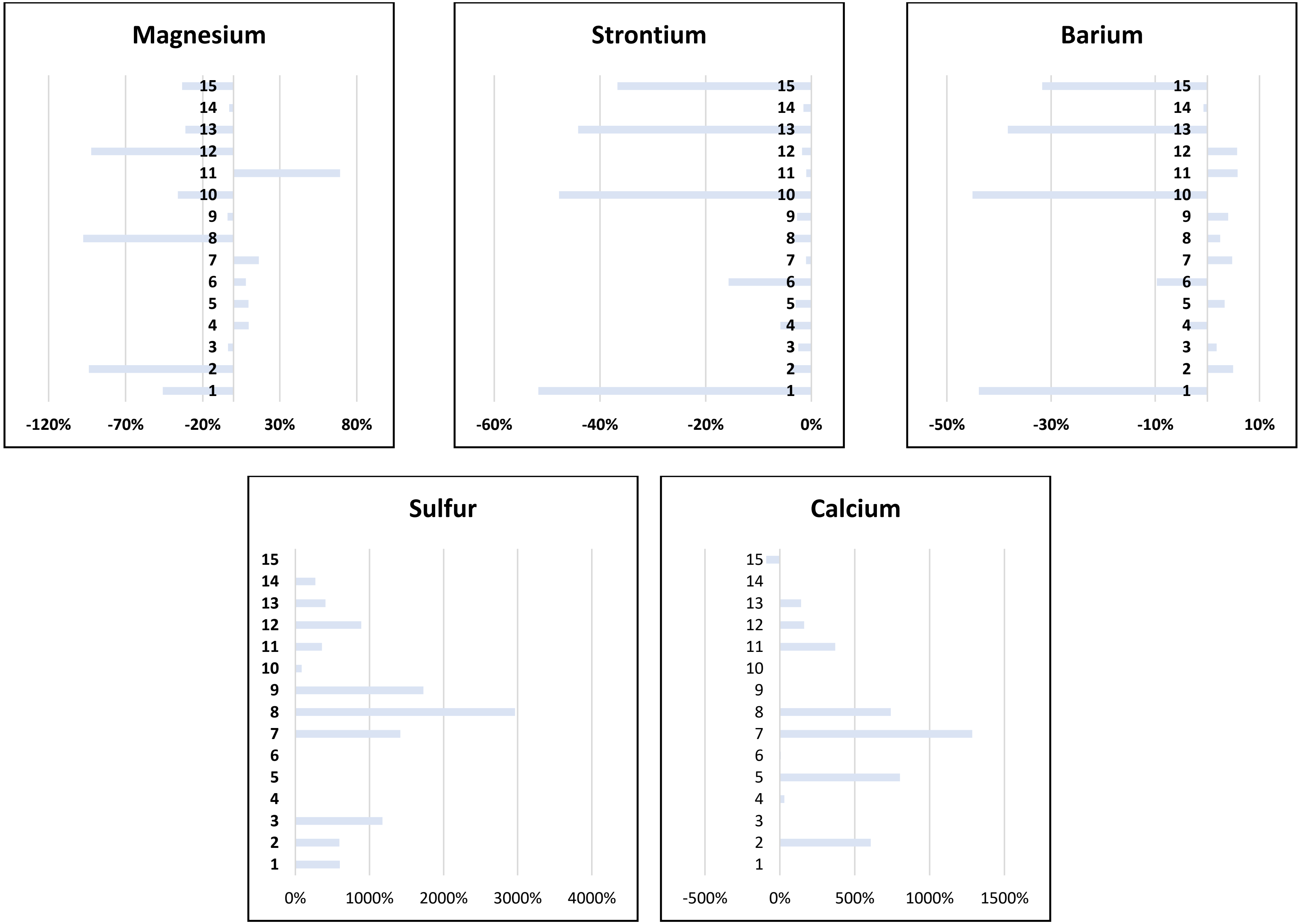

Figure 52: Observed variation amongst elements in initial samples

Table 28: Variation in initial samples (N.D. – Not detected)

StdOrder	Mg	S	Ca	Sr	Ba
1	-46%	602%	N.D.	-52%	-44%
2	-94%	595%	608%	-4%	%
9	-3.6%	1175%	N.D.	-2.5%	1.8%
10	9.9%	N.D.	30%	-5.9%	-3.9%
18	9.8%	N.D.	802%	-3%	3.3%
20	8%	N.D.	7%	-16%	-9.7%
25	16%	1416%	1286%	-1%	4.7%
26	-98%	2963%	741%	-3.5%	2.5%
33	-3.9%	1728%	N.D.	-2.7%	4%
35	-36%	86%	N.D.	-48%	-45%
41	69%	358%	370%	-1%	5.8%
42	-92%	890%	163%	-1.8%	5.7%
49	-31%	407%	142%	-44%	-38%
51	-2.9%	269%	-N.D.	-1.5%	-0.8%
53	-33.%	N.D.	-91%	-37%	-32%

Analysis of samples for final concentrations

Analysis of the measurements made for the final concentrations revealed that in many measurements it was observed that the final concentrations of multiple elements were more than what was originally added at the start of the experiments. Therefore, a check was carried out to quantify the number of such cases. The numbers of such cases for each element is summarized in Figure 54 .

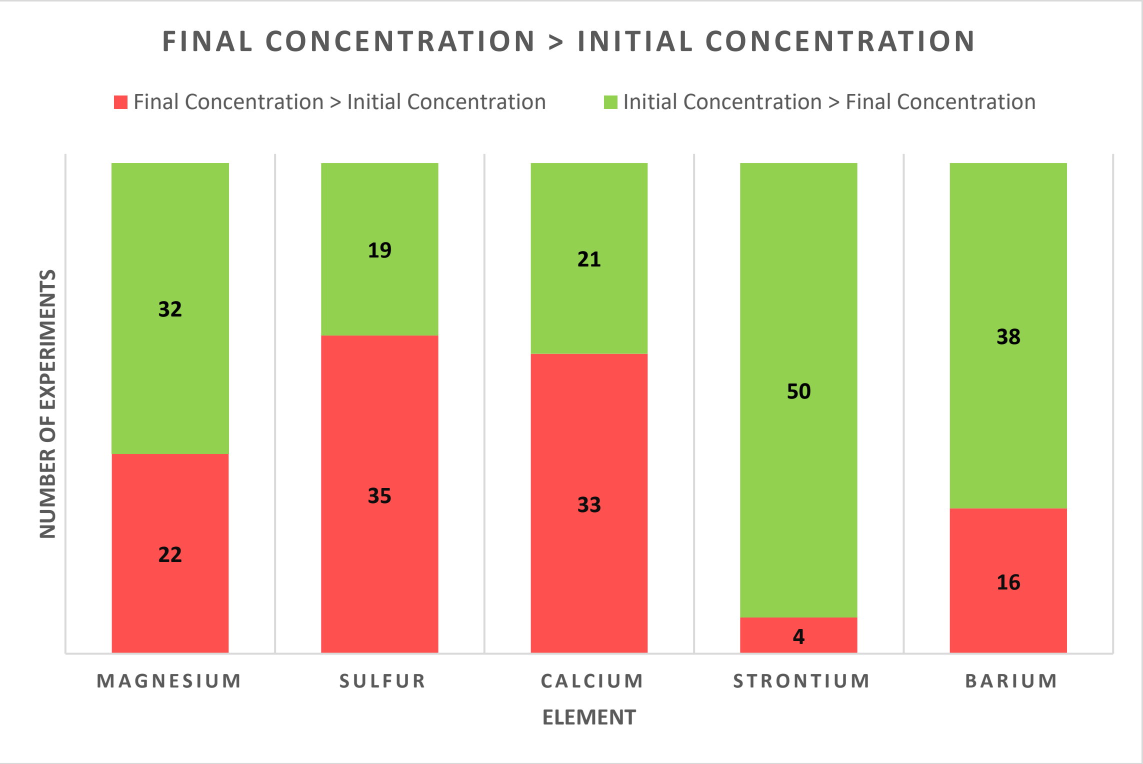

Figure 53: Number of experiments wherein the final concentration is greater than initial concentration

5.3. Proceeding with response analysis

Based on all the information analysed and discussed above, it becomes evident that even in a situation that the OLI simulations performed were not accurate or that there were experimental errors, detection of elements by ICP – MS was not reliable and has resulted in obtaining unusable data.

Given the unreliability of the obtained experimental results, the findings of the OLI simulations remain unvalidated. This, however, is not to say that the predictions made by OLI were proven wrong. A number of practical limitations prevented from experiments being repeated in an improved fashion.

To build a regression model as intended, information about the precipitates formed for each experimental design was needed. Results from OLI simulations were the only data available that had the necessary information to proceed with the regression analysis. Hence, an assumption was made that the predictions made by OLI were reasonably accurate and the data obtained from it could be used to perform the regression analysis.

6. Response Analysis

Chapter Summary: **Based on the outputs from OLI simulation for the designed experiments, the responses were calculated. The calculated responses were analysed used Minitab statistical software. This chapter presents and discusses the outcomes of the response analysis carried out.**

6.1. Responses

The desired responses were calculated using Equation 8 and 9 based on the outcomes of the OLI simulations. The amount of Sr precipitated and the purity of the $SrCO_3$ precipitated for each of the 54 experimental designs can be observed in Table 29 below. The calculated responses were analysed using Minitab.

Table 29: Calculated response values based on OLI simulation

Std. Order	%Sr precipitated	%purity	Std. Order	%Sr precipitated	%purity
1	95.21%	78.01%	**28**	76.33%	32.92%
2	94.22%	31.01%	**29**	88.79%	93.04%
3	71.53%	93.50%	**30**	87.92%	38.60%
4	72.11%	40.76%	**31**	69.39%	69.41%
5	59.44%	39.72%	**32**	76.38%	32.82%
6	69.33%	19.94%	**33**	79.42%	40.57%
7	70.81%	93.45%	**34**	73.88%	74.94%
8	71.65%	40.61%	**35**	80.33%	41.43%
9	72.43%	38.16%	**36**	73.82%	75.09%
10	49.20%	51.05%	**37**	78.71%	32.45%
11	85.47%	29.75%	**38**	72.97%	59.31%
12	86.21%	59.56%	**39**	79.53%	33.01%
13	73.72%	39.17%	**40**	72.89%	59.34%
14	55.65%	47.79%	**41**	62.11%	90.35%
15	85.93%	30.18%	**42**	62.50%	61.14%
16	86.84%	60.33%	**43**	85.87%	65.40%
17	65.67%	66.27%	**44**	88.89%	55.79%
18	98.05%	64.93%	**45**	61.10%	90.22%
19	64.73%	66.49%	**46**	62.51%	20.68%
20	73.71%	45.00%	**47**	85.52%	66.24%
21	64.42%	48.99%	**48**	88.85%	24.72%
22	96.89%	53.62%	**49**	82.10%	51.55%
23	63.54%	48.85%	**50**	82.10%	51.55%
24	73.31%	37.37%	**51**	82.10%	51.55%
25	89.65%	93.21%	**52**	82.10%	51.55%
26	88.14%	38.84%	**53**	82.10%	51.55%
27	67.74%	67.43%	**54**	82.10%	51.55%

6.2. Amount of Sr precipitated (%): Response Surface Regression

On analysing the output of each individual experimental design and comparing it with each component (factors and levels) in that experimental design, a regression equation between the response and the factors is developed. The complete regression equation developed for the amount of Sr precipitated is presented in Equation 12.

$$\begin{aligned}
&\%\mathrm{Sr\ precipitated}\\
&\quad = 0.82098 + 0.01319\,\mathrm{pH} - 0.04004\,\mathrm{Sr} + 0.11581\,\mathrm{C}\\
&\quad - 0.07343\,\mathrm{Ca} + 0.00454\,\mathrm{S} - 0.00364\,\mathrm{Mg} - 0.01314\,\mathrm{pH} * \mathrm{pH}\\
&\quad - 0.04299\,\mathrm{Sr} * \mathrm{Sr} - 0.04073\,\mathrm{C} * \mathrm{C} - 0.00947\,\mathrm{Ca} * \mathrm{Ca} + 0.00703\,\mathrm{S}\\
&\quad * \mathrm{S} - 0.02041\,\mathrm{Mg} * \mathrm{Mg} - 0.00936\,\mathrm{pH} * \mathrm{Sr} + 0.00567\,\mathrm{pH} * \mathrm{C}\\
&\quad + 0.01818\,\mathrm{pH} * \mathrm{Ca} - 0.00118\,\mathrm{pH} * \mathrm{S} + 0.00166\,\mathrm{pH} * \mathrm{Mg}\\
&\quad + 0.05369\,\mathrm{Sr} * \mathrm{C} + 0.07436\,\mathrm{Sr} * \mathrm{Ca} + 0.00206\,\mathrm{Sr} * \mathrm{S} - 0.00038\,\mathrm{Sr}\\
&\quad * \mathrm{Mg} - 0.05763\,\mathrm{C} * \mathrm{Ca} - 0.00829\,\mathrm{C} * \mathrm{S} + 0.00093\,\mathrm{C} * \mathrm{Mg}\\
&\quad + 0.00346\,\mathrm{Ca} * \mathrm{S} + 0.00102\,\mathrm{Ca} * \mathrm{Mg} - 0.00016\,\mathrm{S} * \mathrm{Mg}
\end{aligned} \tag*{Eq. (12)}$$

The input for this equation is in coded form. the This equation is based on the calculations carried out by the software and presented in Table 30. The equation above consists of all terms irrespective of the fact whether they were statistically significant or not. This equation is a summation of the product between the calculated coefficients ("Coef", in Table 30) and their corresponding terms. In brief, the co-efficients are calculated based on averaging the observed responses across the different levels of a factor. These coefficients represent the magnitude and nature of a factor on the response. The larger the magnitude of a co-efficient, the larger is its impact on the studied response. A positive sign of a coefficient implies that the term and the response and positively correlated while a negative sign implies a negative correlation. The effect of factors on the response can be defined in two different ways.

1. Individual/Main Effect – The effect of a factor on a response independent of other factors
2. Interaction Effect – The effect of a factor on a response dependent on the presence and value of other factors.

The summation of these two represent the total effect of a factor on a response. A square effect is used to determine the extent of non-linearity of the effect of a factor on a response.

Along with the co-efficient, p – value for each term is also calculated. A p – value is a probability value that is used to determine the statistical significance of its term. The p – value is representative of the probability that the co-efficient determined is a false positive. The acceptable p – value is based on the targeted confidence level a study aims at. For this study, a p – value of 0.05 was chosen. This corresponds to a confidence level of 95%. Therefore, any term with an associated p – value > 0.05 was considered as insignificant. All significant terms of the model have been highlighted in green in Table 30. Based on Table 30, the complete effect of each factor can be evaluated. Apart from the outputs presented here (Table 30), additional information regarding the developed model is also obtained from the software. This information has to do with additional characteristics of the model. Only outputs relevant for this study are presented. The complete outputs can be checked in the attached software file.

Table 30: Calculated coefficients and their corresponding p – value for all terms associated with the amount of Sr precipitated

Term	Coef	p-value	Term	Coef	p-value
Constant	0.82098	0.000	**Interaction Effects**		
			pH*Sr	-0.00936	0.145
Individual Effects			pH*C	0.00567	0.371
pH	0.01319	0.001	pH*Ca	0.01818	0.000
Sr	-0.04004	0.000	pH*S	-0.00118	0.851
C	0.11581	0.000	pH*Mg	0.00166	0.792
Ca	-0.07343	0.000	Sr*C	0.05369	0.000
S	0.00454	0.218	Sr*Ca	0.07436	0.000
Mg	-0.00364	0.321	Sr*S	0.00206	0.643
			Sr*Mg	-0.00038	0.952
Square Effects			C*Ca	-0.05763	0.000
pH*pH	-0.01314	0.024	C*S	-0.00829	0.194
Sr*Sr	-0.04299	0.000	C*Mg	0.00093	0.834
C*C	-0.04073	0.000	Ca*S	0.00346	0.584
Ca*Ca	-0.00947	0.097	Ca*Mg	0.00102	0.871
S*S	0.00703	0.212	S*Mg	-0.00016	0.979
Mg*Mg	-0.02041	0.001			

- pH has a significant positive effect on the amount of Sr precipitated. This is primarily due to the fact that precipitation of $SrCO_3$ occurs only in the alkaline range. The magnitude of the effect of pH is not relatively high due to the choice of range of study (alkaline range).
- Sr has a significant negative effect on the amount of Sr precipitated. While it might seem counterintuitive that a higher Sr concentration would have a negative impact on the total Sr precipitated, it must be taken into consideration that the amount of C remains constant in the system. Therefore, beyond a certain Sr value, no $SrCO_3$ precipitation takes place due to lack of C and a further increase in Sr reduces the total amount of Sr precipitated i.e. the numerator of Equation 8 remains constant while the denominator keeps increasing.
- C has a significant positive impact on the amount of Sr precipitated. The magnitude of the effect of C is the largest of all individual factors. This is primarily because almost all of the Sr is being precipitated as $SrCO_3$. Therefore, irrespective of the amount of Sr present in the system, it is C that behaves as a limiting agent and hence has the highest magnitude of impact amongst all effects.
- Ca has a significant negative effect on the amount of Sr precipitated. The negative effect of Ca can be attributed to the formation of $CaCO_3$. Due to formation of $CaCO_3$ precipitates, the total amount of C available for $SrCO_3$ precipitation reduces. Thus, lesser amounts of Sr can precipitate as $SrCO_3$.
- S has a low positive effect on the amount of Sr precipitated. The positive effect could be either due to the precipitation of $SrSO_4$ or due to reduction in total available Ca (due to formation of Ca – S species) which would allow for more $SrCO_3$ to precipitate. However, the effect of S is insignificant in the range of study. The effect of S being insignificant could be attributed to the range of pH chosen. This pH range is not favourable for $SrSO_4$ to precipitate and hence only one out of the 54 responses show $SrSO_4$ precipitation.

- Mg has a low negative and insignificant impact on the total amount of Sr precipitated. As seen in Figures 13 - 14, the presence of Mg has no effect on $SrCO_3$ precipitation. Therefore, Mg has no equilibrium-based effect on the total amount of Sr precipitated and hence is insignificant.
- A significant square term indicates that the relationship between the concerned factor and the response follows a curved line (as opposed to a linear). From the p-values it can be seen that the square terms of pH, Sr, C and Mg are significant indicating they have a nonlinear (curved) effect on the amount of Sr precipitated. The significance of the square effect for Mg could be attributed to the reduction in the amount of hydroxyl ions (OH^-) due to precipitation as $Mg(OH)_2$, which in turn could reduce the pH and hence have a negative impact on the amount of Sr precipitated.

The variation in the response attributable just to the individual effects of each factor is plotted in Figure 55. If a sizeable difference in the response (blue line) is observed on variation of the factor (x – axis), then that factor is considered as significant.

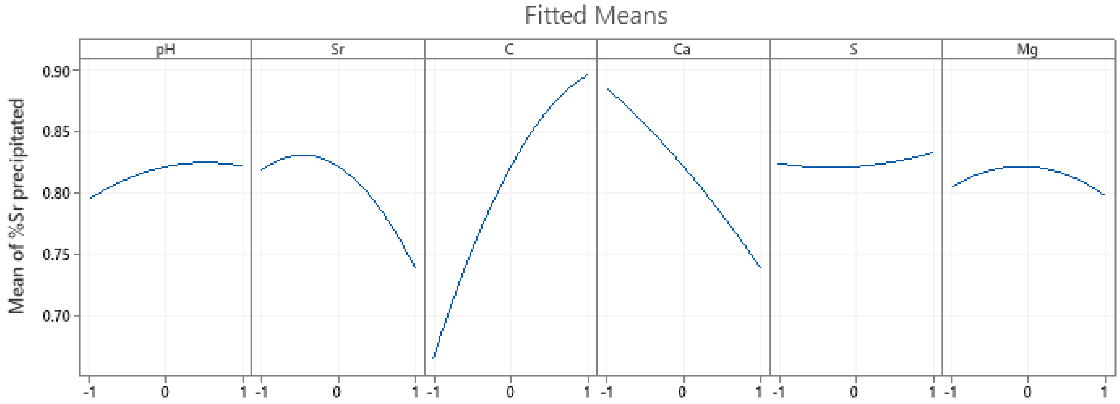

Figure 54: Main effect plots for the fitted values of "Amount of Sr Precipitated %"

The presence of a significant interaction effect implies that the effect of a factor on the response is dependent on other factors (at the levels/values of these factors) as well. From Table 30 it is observed that the significant interaction effects include pH – Ca, Sr – C, Sr – Ca and C – Ca.

- pH and Ca have a positive interaction effect on the amount of Sr precipitated. This would imply that when pH is increased, the negative effect of Ca is reduced (i.e. becomes more positive) and vice versa.
- Sr and C have a positive interaction effect on the amount of Sr precipitated. The effect can be understood explained as both these facts are the driving forces for the precipitation of $SrCO_3$. Increasing one of the components would result in formation of more $SrCO_3$ which would increase the amount of Sr precipitated.
- Sr and Ca have a positive interaction effect on the amount of Sr precipitated which can be observed. This positive interaction implies that the presence of either Sr or Ca reduces the negative individual impact of the other. Based on the similar nature of Sr and Ca, it would be expected that they would compete and hence have a negative interaction effect. However, the findings based on the regression equation indicate otherwise.
- C and Ca present the only negative interaction effect which is also significant. The negative interaction effect implies that if either C or Ca are increased in concentration then their overall effect on the response shifts more towards the negative end. For example, if Ca is increased at a constant value C, then the probability of formation of $CaCO_3$ increases. This reduces the total

amount of C available for precipitation of $SrCO_3$ and hence reduces the total amount of Sr precipitated. The increase in Ca results in reduction of C which reduces its effect.

The interaction effects amongst all pairs of factors are plotted in Figure 57. These plots can also be used to evaluate the significance of interaction factors. The significant interaction factors can be identified if the response (represented by the lines in each plot) varies across different levels of the factor (y-axis) for all levels of the other factor.

The equation has a R^2 value of 98.75% indicating that 98.75% of the variability in the responses (calculated based on the regression equation) can be explained by the variability of the factors. The complete model has a predictive R^2 of 93.45 % which is a measure of how well the model the model predicts responses for new observations. Apart from the R^2 value, the adequacy/goodness – of – fit of the developed model can be verified by the residual plots as presented in Figure 56. A residual is defined as the difference between the observed value (in this case the response predicted using OLI) and the value predicted through the developed regression model. Each plot is interpreted in a unique manner and helps determine if the coefficients estimated are biased or not. The residual plot is to be interpreted as follows:

1. Normal Probability Plot: This is used to determine whether the residuals are normally distributed or not. The residuals should fall on a straight line, the failure of which could indicate nonnormality, presence of an outlier or the presence of an unidentified outlier.
2. Versus Fits: This is used to visualize whether the variance of the residuals is uniform or not
3. Histogram: This is used to identify the skewness of the data along with the presence of outliers
4. Versus Order: This is used to check the presence of correlation between different residuals.

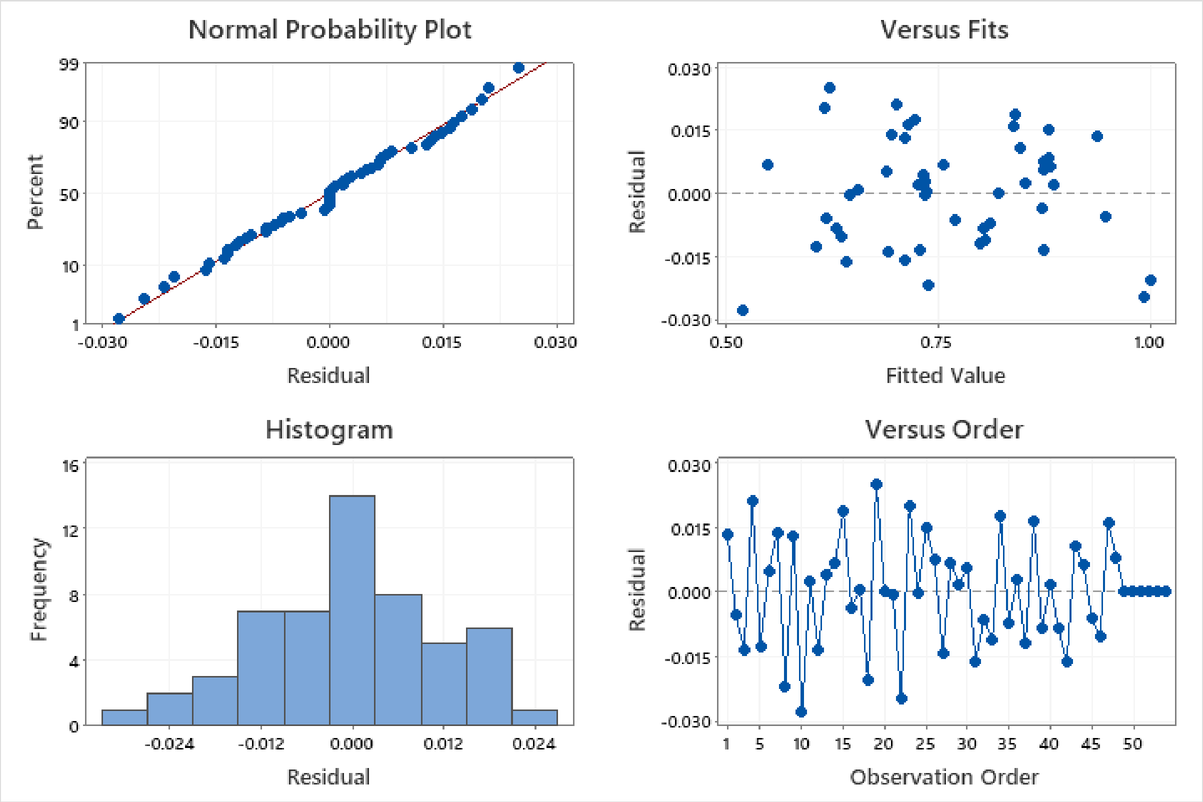

Figure 55: Residual Plots for the response, Amount of Sr precipitated (%)

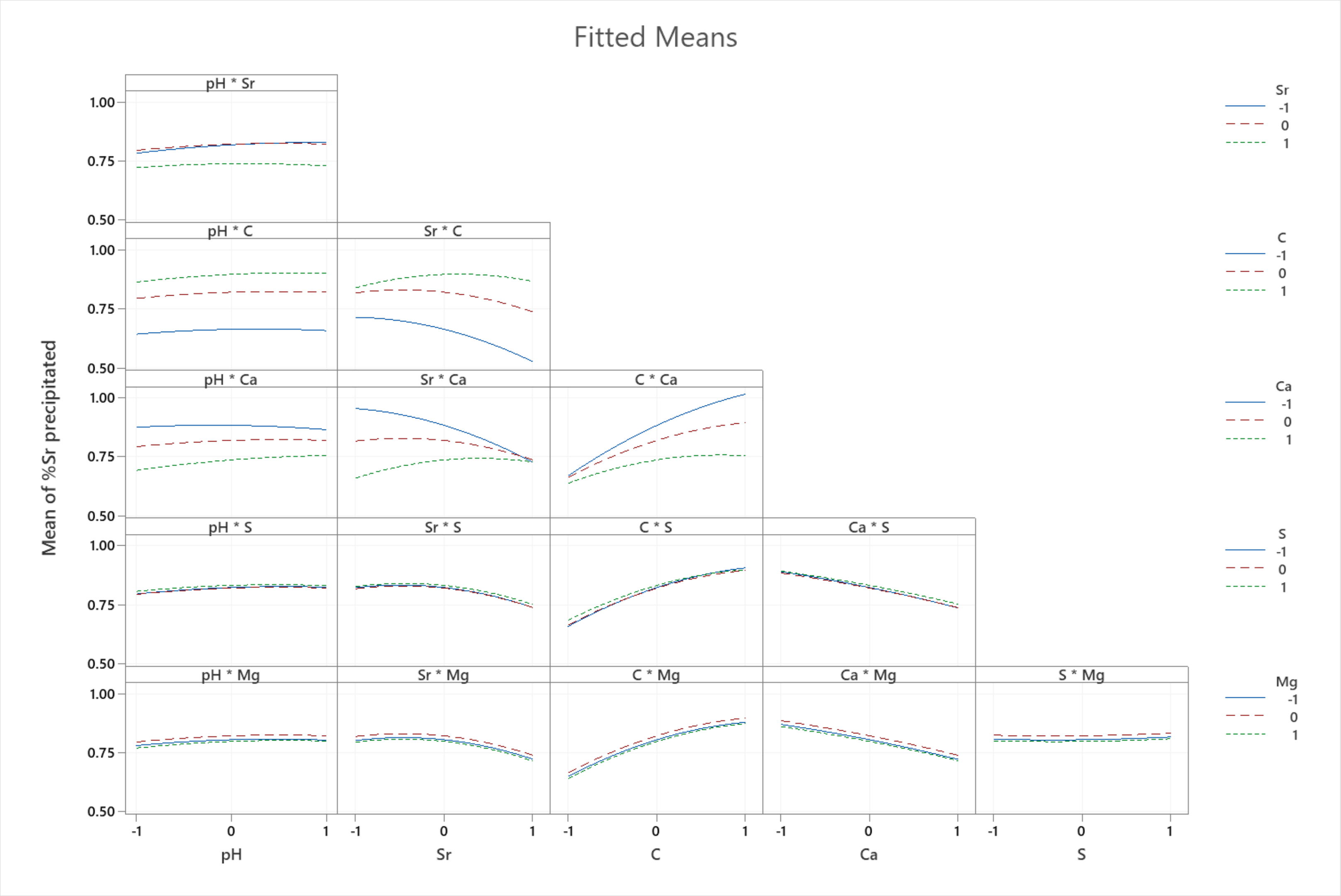

Figure 56: Interaction plots for the amount of Sr precipitated for all factors

From figure 56, it can be seen that (i) The “Normal Probability Plot” follows an almost straight line (ii) The “Versus Fits” plot has no discernible patter (iii) The “Histogram” shows no skewness and (iv) The “Versus Order” has no trend/pattern except for the last few points.

The “Versus Order” plot shows the last few point showing a pattern. This can be explained by the fact that these points represent the centre points of the design i.e. identical experimental designs. Since the responses are obtained via simulation, their values are identical and hence follow a pattern. Therefore, through the residual plots it is established that the developed regression model is adequate and meets the various assumptions of the analysis carried out.

Based on the significance of each individual term, the complete equation can be shortened to one consisting only of significant terms. The shortened equation can be seen in Equation 13. The shortened equation has as R^2 value of 98.01% indicating its good fit. This shortened equation can be used to perform predictive analysis for the amount of Sr precipitated based on the factors of pH, Sr, C, Ca, S and Mg.

$$\begin{aligned}
&\%\mathrm{Sr\ precipitated}\\
&\quad = 0.82098 + 0.01319\,\mathrm{pH} - 0.04004\,\mathrm{Sr} + 0.11581\,\mathrm{C} - 0.07343\,\mathrm{Ca}\\
&\quad - 0.01314\,\mathrm{pH} * \mathrm{pH} - 0.04299\,\mathrm{Sr} * \mathrm{Sr} - 0.04073\,\mathrm{C} * \mathrm{C}\\
&\quad - 0.02041\,\mathrm{Mg} * \mathrm{Mg} + 0.01818\,\mathrm{pH} * \mathrm{Ca} + 0.05369\,\mathrm{Sr} * \mathrm{C}\\
&\quad + 0.07436\,\mathrm{Sr} * \mathrm{Ca} - 0.05763\,\mathrm{C} * \mathrm{Ca}
\end{aligned} \qquad \text{Eq. (13)}$$

6.3. $SrCO_3$ purity (%): Response Surface Regression

This section presents and discusses the outcome for the analysis on the second response of interest, the purity of $SrCO_3$ precipitated. Equation 14 represents the complete regression equation for the purity of the $SrCO_3$ precipitated. The input for this equation is in coded form. The p-value associated with each term can be found in Table 31.

$$\begin{aligned}
&\mathrm{SrCO_3\ purity\ (\%)}\\
&\quad = 0.5155 - 0.20923\,\mathrm{pH} + 0.12593\,\mathrm{Sr} - 0.03178\,\mathrm{C}\\
&\quad - 0.06115\,\mathrm{Ca} + 0.00087\,\mathrm{S} - 0.07187\,\mathrm{Mg} + 0.0617\,\mathrm{pH} * \mathrm{pH}\\
&\quad - 0.0388\,\mathrm{Sr} * \mathrm{Sr} - 0.0295\,\mathrm{C} * \mathrm{C} + 0.0079\,\mathrm{Ca} * \mathrm{Ca} - 0.0022\,\mathrm{S} * \mathrm{S}\\
&\quad + 0.0456\,\mathrm{Mg} * \mathrm{Mg} - 0.0485\,\mathrm{pH} * \mathrm{Sr} + 0.0595\,\mathrm{pH} * \mathrm{C} + 0.0405\,\mathrm{pH}\\
&\quad * \mathrm{Ca} - 0.0027\,\mathrm{pH} * \mathrm{S} - 0.0903\,\mathrm{pH} * \mathrm{Mg} + 0.0481\,\mathrm{Sr} * \mathrm{C}\\
&\quad + 0.0614\,\mathrm{Sr} * \mathrm{Ca} - 0.0032\,\mathrm{Sr} * \mathrm{S} - 0.0184\,\mathrm{Sr} * \mathrm{Mg} - 0.0453\,\mathrm{C}\\
&\quad * \mathrm{Ca} + 0.0043\,\mathrm{C} * \mathrm{S} + 0.0165\,\mathrm{C} * \mathrm{Mg} + 0.0029\,\mathrm{Ca} * \mathrm{S} + 0.0042\,\mathrm{Ca}\\
&\quad * \mathrm{Mg} - 0.0006\,\mathrm{S} * \mathrm{Mg}
\end{aligned} \qquad \text{Eq. (14)}$$

- All factors have a significant individual effect with the exception of S. The effect of S is low in magnitude and insignificant.
- Of all the significant individual effects, Sr is the only one to have a positive individual effect on the response. This is primarily because increasing the amount of Sr would result in a larger amount of $SrCO_3$ being precipitated and hence increase its proportion in the total amount of precipitates formed.
- pH had the highest magnitude of all individual impacts. This along with its effect being negative can be attributed to the reason that as pH increases, increased precipitation of $CaCO_3$ and

$Mg(OH)_2$ is observed in addition to that of $SrCO_3$. This reduces the proportion of $SrCO_3$ in the total amount of precipitates formed and hence is causing a negative effect.

Table 31: Calculated coefficients and their corresponding p-value for all terms associated with the purity of $SrCO_3$ precipitated

Term	Coef	p-value	Term	Coef	p-value
Constant	0.5155	0.000	**Interaction Effects**		
			pH*Sr	-0.0485	0.006
Individual Effects					
pH	-0.20923	0.000	pH*C	0.0595	0.001
Sr	0.12593	0.000	pH*Ca	0.0405	0.001
C	-0.03178	0.002	pH*S	-0.0027	0.870
Ca	-0.06115	0.000	pH*Mg	-0.0903	0.000
S	0.00087	0.926	Sr*C	0.0481	0.006
Mg	-0.07187	0.000	Sr*Ca	0.0614	0.001
			Sr*S	-0.0032	0.782
Square Effects			Sr*Mg	-0.0184	0.262
pH*pH	0.0617	0.000	C*Ca	-0.0453	0.009
Sr*Sr	-0.0388	0.011	C*S	0.0043	0.792
C*C	-0.0295	0.047	C*Mg	0.0165	0.159
Ca*Ca	0.0079	0.582	Ca*S	0.0029	0.860
S*S	-0.0022	0.879	Ca*Mg	0.0042	0.798
Mg*Mg	0.0456	0.003	S*Mg	-0.0006	0.968

- C is shown to have a negative effect. The effect is low in magnitude. The negative nature of the effect is potentially due to increased/greater $CaCO_3$ precipitation at higher levels of C.
- Ca and Mg, as expected, have a negative effect on the purity of $SrCO_3$ precipitated. The magnitude of the effect is slightly higher for Mg in comparison to Ca. The choice of pH range for this study could be the reason for the same as it could promote more $Mg(OH)_2$ precipitation as compared to $CaCO_3$ precipitation.
- pH, Sr, C and Mg also show significant square effects indicating that their effect on the purity of $SrCO_3$ purity follows a non – linear trend. The absence of a significant square effect for Ca indicates that the relationship between Ca and the purity of $SrCO_3$ is linear in nature.

The individual effects of each factor of the purity of $SrCO_3$ precipitated can be seen in Figure 58. Out of all possible interaction effects, the significant ones include pH – Sr, pH – C, pH – Ca, pH – Mg, Sr – C, Sr – Ca and C – Ca.

- The negative interaction effect between pH and Sr could be explained by the increase in OH^- ions (associated with higher pH) which could form species with Sr and reduce the total amount of Sr available to precipitate as $SrCO_3$

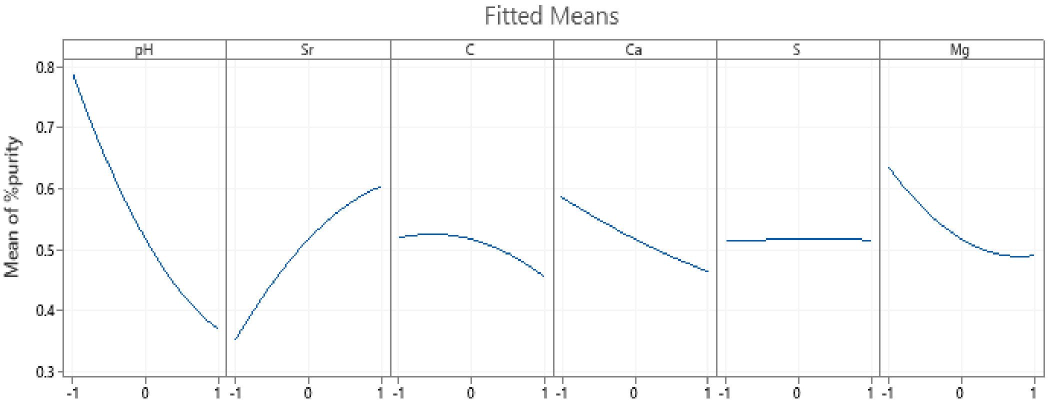

Figure 57: Main effect plots for the fitted values of "Amount of Sr Precipitated %"

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- Similarly, for pH – Mg interaction, the increase in pH results in more OH^- ions which result in higher $Mg(OH)_2$ precipitation, decreasing the purity of the $SrCO_3$ precipitated.
- The negative nature of C - Ca can be explained by the fact that if either one of them were to increase, it would lead to increased $CaCO_3$ precipitation thereby reducing the purity of $SrCO_3$ precipitated.
- Sr and C represent the driving force for the precipitation of $SrCO_3$. Therefore, an increase of either would lead to increased $SrCO_3$ precipitation resulting in a higher proportion of $SrCO_3$ precipitate in the total amounts of precipitate formed, thereby justifying its positive interaction effect.
- The positive interaction effect between pH – C can be understood as the increase in pH facilitating a larger amount of C to speciate as CO_3^{2-}. Higher CO_3^{2-} in the solution would allow for more Sr to precipitate as $SrCO_3$ thereby increasing the purity of $SrCO_3$ precipitated.
- A positive interaction effect between pH – Ca can be explained by the speciation between Ca and OH^- ions. Higher pH values result in more hydroxyl ions. These hydroxyl ions speciate with Ca to form $Ca(OH)^+$. This speciation results in a reduced amount of Ca available to precipitate as $CaCO_3$. This would have a twofold effect as this would allow for more $SrCO_3$ to be precipitated while at the same time reducing the amount $CaCO_3$ precipitating, thereby increasing the purity of $SrCO_3$ precipitated.
- Similar to what was observed in the case of the first response (amount of Sr precipitated), a positive interaction effect was observed between Sr and Ca. Sr an Ca being similar in nature should theoretically compete with one another for the C in the solution and therefore have a negative interaction effect.

The interaction effects amongst all pairs of factors are plotted in Figure 59. The equation has a R^2 value of 97.38% indicating that 97.38% of the variability in the responses (calculated based on the regression equation) can be explained by the variability of the factors. The complete model has a predictive R^2 of 86.32 % which is a measure of how well the model the model predicts responses for new observations. Figure 58 represents the residual plots for the developed regression model describing $SrCO_3$ purity. From the residual plots it can be seen that (i) The "Normal Probability Plot" follows a straight line (ii) The "Versus Fits" plot has no discernible pattern (iii) The "Histogram" follows the pattern of a standard normal distribution and (iv) The "Versus Order" has a random pattern[24]. Thus, seeing that all four

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[24] The last few points have an identical residual as they are exact replicates obtained via OLI, i.e. no randomness

residual plots do not present any unusual behaviour, the model can be described as adequate.

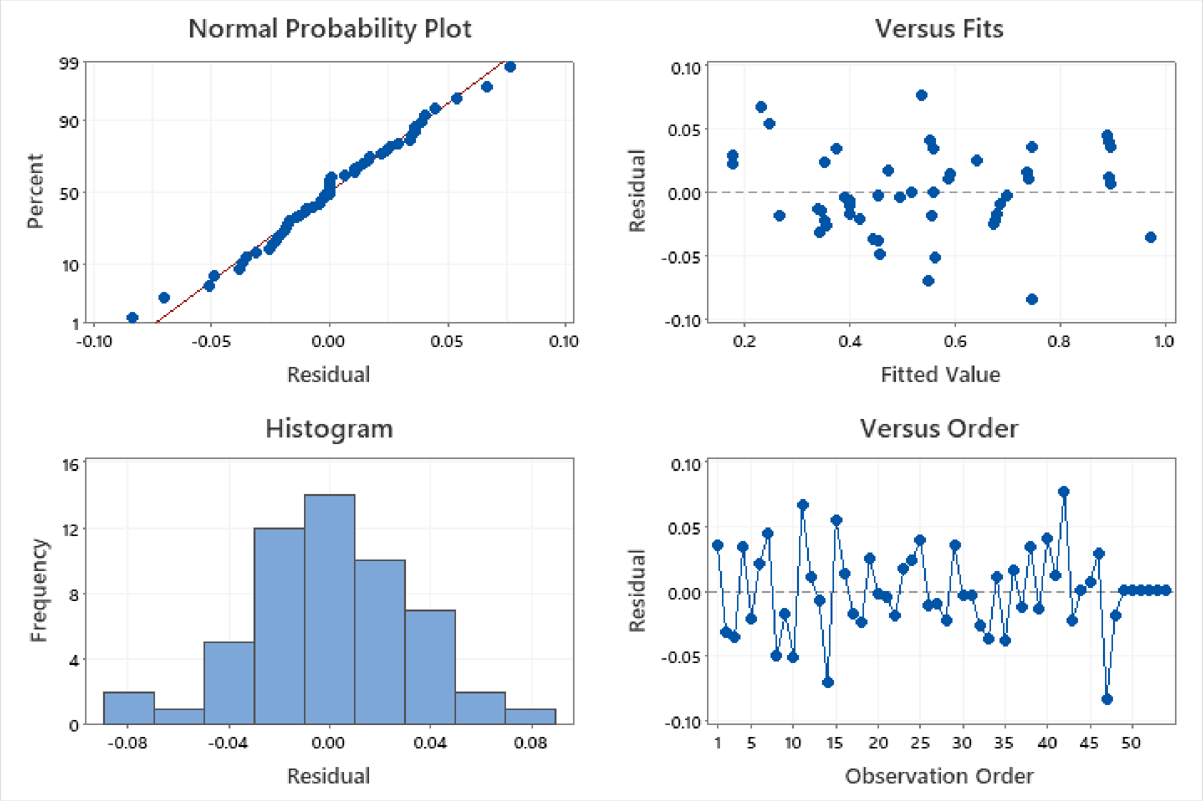

Figure 58: Residual Plots for the response, Purity of $SrCO_3$ precipitated (%)

Based on the significance of each individual term, the complete equation can be shortened to one consisting only of significant terms. The shortened equation can be seen in Equation 15. The shortened equation has as R^2 value of 85.41% indicating how well it fits.

$$\begin{aligned} \mathrm{SrCO_3\ purity\ (\%)} \\ &= 0.5155 - 0.20923\,\mathrm{pH} + 0.12593\,\mathrm{Sr} - 0.03178\,\mathrm{C} \\ &- 0.06115\,\mathrm{Ca} - 0.07187\,\mathrm{Mg} + 0.0617\,\mathrm{pH} * \mathrm{pH} - 0.0388\,\mathrm{Sr} * \mathrm{Sr} \\ &- 0.0295\,\mathrm{C} * \mathrm{C} + 0.0456\,\mathrm{Mg} * \mathrm{Mg} - 0.0485\,\mathrm{pH} * \mathrm{Sr} + 0.0595\,\mathrm{pH} \\ &* \mathrm{C} + 0.0405\,\mathrm{pH} * \mathrm{Ca} - 0.0903\,\mathrm{pH} * \mathrm{Mg} + 0.0481\,\mathrm{Sr} * \mathrm{C} \\ &+ 0.0614\,\mathrm{Sr} * \mathrm{Ca} - 0.0453\,\mathrm{C} * \mathrm{Ca} \end{aligned} \qquad \text{Eq. (15)}$$

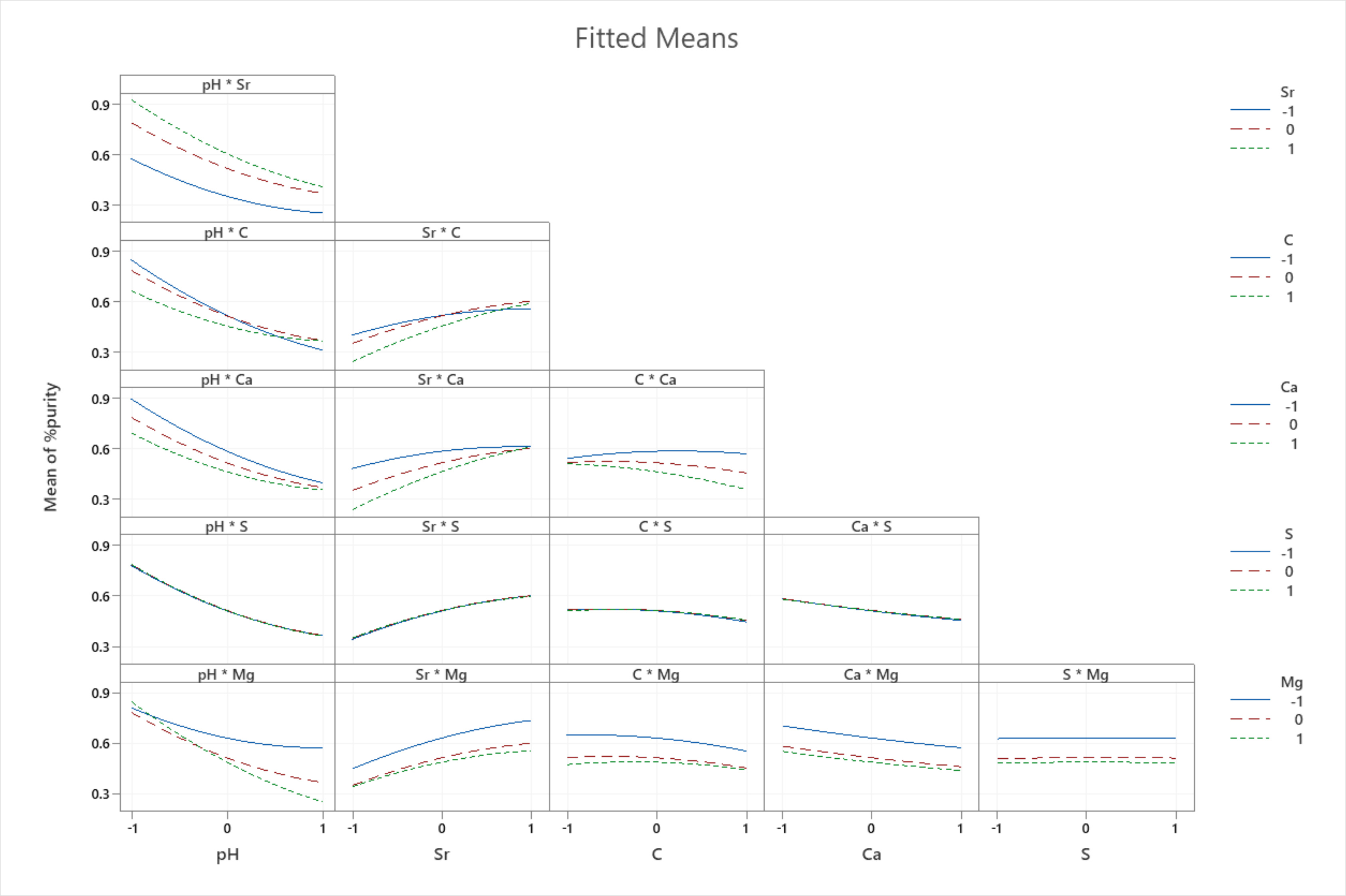

Figure 59: Interaction plots for the purity of $SrCO_3$ precipitated

7. Conclusions

The recovery of Sr from concentrate as $SrCO_3$ via precipitation was explored in this study. A Box-Behnken Design (BBD) was implemented to develop regression equations describing the amount of Sr precipitating and the purity of $SrCO_3$ precipitated in an aqueous solution. These regression equations were built based on theoretical knowledge, explorative OLI simulations and conditions observed in concentrate produced at the drinking water facility of PWN.

Existing theoretical knowledge, supported by OLI simulations indicated that pH and concentrations of strontium (Sr), inorganic carbon (C), calcium (Ca), barium (Ba), magnesium (Mg) and inorganic sulphur (S) could have an effect on the equilibrium conditions surrounding the precipitation of $SrCO_3$. All variable with the exception of Mg was hypothesized to have both, a qualitative and quantitative effect on $SrCO_3$ precipitation. Mg was hypothesized to have only a qualitative effect.

The relatively low concentration of Sr in concentrate produced at PWN made it impractical to facilitate its direct recovery. A pre-treatment scheme was investigated through OLI simulations which would make the recovery of Sr from the concentrate feasible. This pre-treatment scheme was based only on the variation of process conditions (pH, temperature and pressure). Through the proposed pre-treatment, simultaneous recovery of $CaCO_3$, $Mg(OH)_2$ and $Ca(OH)_2$ is possible. Subject to the investigated pre – treatment scheme it is theoretically possible to recover over 2 tonnes of $SrCO_3$ annually. The overview of the recovered resources is presented in Table 20.

Table 20: Overview of the recovered resources

Resource	Recovered amount	Purity	Recovery Rate	Annual recovered amount
	g/L concentrate			Tonnes/year
$CaCO_3$	0.684	99.95%	97.12%	1006.6
$Mg(OH)_2$	0.161	96%	99.99%	236.94
$Ca(OH)_2$	0.0083	99.99%	82.4%	12.21
$SrCO_3$	0.0014	100%	60.16%	2.06

Through the information ascertained by the above activities, a Box – Behnken Design was designed to evaluate the $SrCO_3$ precipitation in an aqueous solution. The design evaluated the amount of Sr recovered and the purity of $SrCO_3$ precipitated. The design was based on six factors, pH, Sr, C, Ca, Mg and S and evaluated. The range of each factor is presented in Table 22.

Table 22: Levels chosen for BBD

Factor	Unit	-1	0	1
pH	-	9	11	13
Sr	*mM*	0.5	0.75	1
C	*mM*	0.5	0.75	1
Ca	*mM*	0.25	1	1.75
S	*mM*	0.25	1	1.75
Mg	*mM*	0.25	1	1.75
Ba	*mM*		0.05	

Measurements and data needed for the design were obtained through OLI simulations. Experiments were performed to validate the OLI simulations. However, the experiments were not successful due to errors in detection coupled with one potential unaccounted external factor. Equations 13 and 15 represent the regression model associating the amount of Sr precipitated and the purity of $SrCO_3$ precipitated respectively.

$$\begin{aligned} \%\mathrm{Sr\ precipitated} &\\ = {} & 0.82098 + 0.01319\,\mathrm{pH} - 0.04004\,\mathrm{Sr} + 0.11581\,\mathrm{C} - 0.07343\,\mathrm{Ca} \\ & - 0.01314\,\mathrm{pH} * \mathrm{pH} - 0.04299\,\mathrm{Sr} * \mathrm{Sr} - 0.04073\,\mathrm{C} * \mathrm{C} - 0.02041\,\mathrm{Mg} * \mathrm{Mg} \\ & + 0.01818\,\mathrm{pH} * \mathrm{Ca} + 0.05369\,\mathrm{Sr} * \mathrm{C} + 0.07436\,\mathrm{Sr} * \mathrm{Ca} - 0.05763\,\mathrm{C} * \mathrm{Ca} \end{aligned}$$

$$\begin{aligned} \mathrm{SrCO_3\ purity\ (\%)} &\\ = {} & 0.5155 - 0.20923\,\mathrm{pH} + 0.12593\,\mathrm{Sr} - 0.03178\,\mathrm{C} - 0.06115\,\mathrm{Ca} \\ & - 0.07187\,\mathrm{Mg} + 0.0617\,\mathrm{pH} * \mathrm{pH} - 0.0388\,\mathrm{Sr} * \mathrm{Sr} - 0.0295\,\mathrm{C} * \mathrm{C} \\ & + 0.0456\,\mathrm{Mg} * \mathrm{Mg} - 0.0485\,\mathrm{pH} * \mathrm{Sr} + 0.0595\,\mathrm{pH} * \mathrm{C} + 0.0405\,\mathrm{pH} * \mathrm{Ca} \\ & - 0.0903\,\mathrm{pH} * \mathrm{Mg} + 0.0481\,\mathrm{Sr} * \mathrm{C} + 0.0614\,\mathrm{Sr} * \mathrm{Ca} - 0.0453\,\mathrm{C} * \mathrm{Ca} \end{aligned}$$

The adequacy of the built models was verified through residual plots (Figure 56 and 58). The summary of the models is presented in Table 32.

Table 32: Summary of models developed

	R^2	**Predictive R^2**
% Sr precipitated		
Full Equation	98.75%	93.45%
Significant Terms only	98.01%	
$SrCO_3$ purity (%)		
Full Equation	97.38%	86.32%
Significant Terms only	85.41%	

The complete significant effect of each factor is presented in Table 33. S was shown to have no significant impact on the amount of Sr precipitated or the purity of $SrCO_3$ precipitated based on the chosen range of study. The positive interaction effect between Sr – Ca on both the responses was the only effect that could not be supported based on available theoretical knowledge.

Table 33: Significant effect of each studied factor on the chosen response

Factor	**% Sr precipitated**	**$SrCO_3$ purity (%)**
pH	(0.01319 – 0.01314 pH + 0.01818 Ca) * pH	(-0.20923 + 0.0617 pH – 0.0485 Sr + 0.0595 C + 0.0405 Ca – 0.0903 Mg) * pH
Sr	(- 0.04004 – 0.04299 Sr + 0.05369 C + 0.07436 Ca) * Sr	(0.12593 – 0.0388 Sr – 0.0485 pH + 0.0481 C + 0.0614 Ca)* Sr
C	(0.11581 – 0.04073 C + 0.05369 Sr – 0.05763 Ca) * C	(-0.03178 – 0.0295 C + 0.0595 pH + 0.0481 Sr – 0.0453 Ca) * C
Ca	(-0.07343 + 0.01818 pH – 0.05763 C) * Ca	(-0.06115 + 0.0405 pH + 0.0614 Sr – 0.0453 C) * Ca
S	-	-
Mg	(-0.02041 Mg)*Mg	(-0.07187 + 0.0456 Mg – 0.0903 pH) * Mg

7.1. Recommendations

Tasks carried out to reach the conclusions of this study were based on researched information and practical assumptions. While this implies that the findings of this report are reliable subject to the considerations taken into account, certain additional activities can be undertaken to enhance the robustness of these findings.

1. Inclusion of coprecipitation and formation of solid solutions would increase the representativeness of the findings to what could be realistically observed. The effect of coprecipitation and formation of solid solutions would improve the accuracy of OLI simulated predictions and if a considerable difference is observed, it could influence the significance of the developed model.
2. The effect of NOM should be evaluated with more types, especially the more prominent ones such as humic acids and fulvic acids.
3. The pre – treatment of PWN concentrate can be improved by:
   - 3.1. Having actual measurements of Mg in the concentrate as opposed to IMSDesign simulations
   - 3.2. Giving due consideration to the effect of anti-scalants present in the concentrate
   - 3.3. Making calculations taking into account the range of different ions in the concentrate rather than just the averages.
   - 3.4. Exploring pre-treatment steps through other mechanisms such as addition of reagents, employing, ion exchange etc and coupling it with the variation of process conditions.
   - 3.5. Choosing the most suitable outcomes on less subjective criteria
4. Quality analysis should be carried out on different concentrates so as to ensure that the range(levels) of the experimental design have increased practical applicability.
5. Experiments should be performed with a revised protocol to ensure they work out and can be used to check the validity of the OLI simulations. A revised protocol is presented in Appendix 9.8.
6. BBD can be redesigned with the exclusion of S as a factor. This would allow for the regression output to be more significant in nature. Alternatively, a CCD can also be implemented, and the differences observed, if any, can be evaluated. On similar line, the levels of each factor can be readjusted to broaden the specificity of the outcomes.

7.2. Scope for the future

In addition to considering steps to increase the robustness and applicability of this study's findings, certain steps can also allow to expand on what has been studied.

1. The findings of this study are based majorly on theoretical information. Experiments need to be performed to identify the difference between what is predicted and what is observed. The new information would allow for developing a better model.
2. The simulations performed and results are based on final equilibrium conditions. The kinetics of the process can also have a major influence on decision making. Performing kinetic studies or inclusion of kinetic considerations will provide a more complete picture.
3. Similar mathematical models can be built for mechanisms such as co-precipitation and can be incorporated into the main findings as a correction factor or extensions.

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9. Appendix

9.1. Additional files

Additional files have been submitted along with this report. Information present in these files were adapted into this report.

Sr.No.	**Document Name**	**Explanation**
1	PWN UF Effluent - 218	IMSDesign simulation performed to obtain missing Mg^{2+} concentration
2	Selection of Factors	OLI file containing simulations to identify important factors for $SrCO_3$ precipitation
3	Pre – treatment of concentrate	OLI file used to explore the pre – treatment of concentrate
4	Pre – treatment_Data Points	Excel sheet containing data extracted from OLI file "Pre – treatment of concentrate"
5	Experimental Results and Conversions	Excel file containing experimental results and transformation of data
6	$SrCO_3$ precipitation - OLI	OLI file used to perform DOE
7	$SrCO_3$ precipitation - BBD	Minitab file used to perform DOE

9.2. Identification of Relevant Factors – OLI Simulations

Subsections 9.2.2. – 9.2.4. contain the graphical outputs for simulations run at a fixed value of 0.1 mM, 10 mM and 100 mM respectively. These graphs are to be interpreted in the same fashion as described in Chapter 2 for a fixed value of 1 mM. Therefore, no additional details (outside the graphical results) are provided.

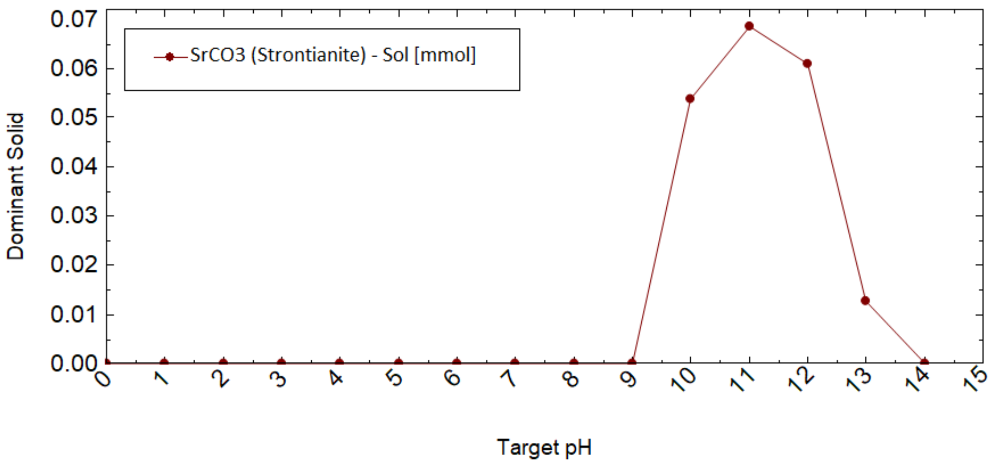
9.2.1. Step – by – step procedure

- Open blank OLI file.
- Go to "Streams", select option "Add stream". A blank input box (default name – Stream) is created on the left side of the screen.
- Add desired inflows. Concentration of inflows can be adjusted later. Adjust units of input and output to the desired ones. Select choice of chemistry/thermodynamic model. For this study "MSE (H_3O^+ ion)" was chosen
- Select "Add calculation" option on right side of the screen. Selection option of "Survey"
- Open new input box (default name – "Survey"). Adjust input values to what is desired.
- On the right side panel "Survey by" adjust variable to be varied/manipulated. For a single survey only one variable has to be selected while for a dual survey two variables need to be considered.
- Select "Specs" option to adjust the range and step size of the survey. Adjust the start point, end point and step size.
- Press "Calculate" for simulation to run. If some important information is missing the "Calculate" option cannot be selected.
- After simulation is run, the visual output can be seen in "Plot" tab and more specific details can be seen in "Report" tab.

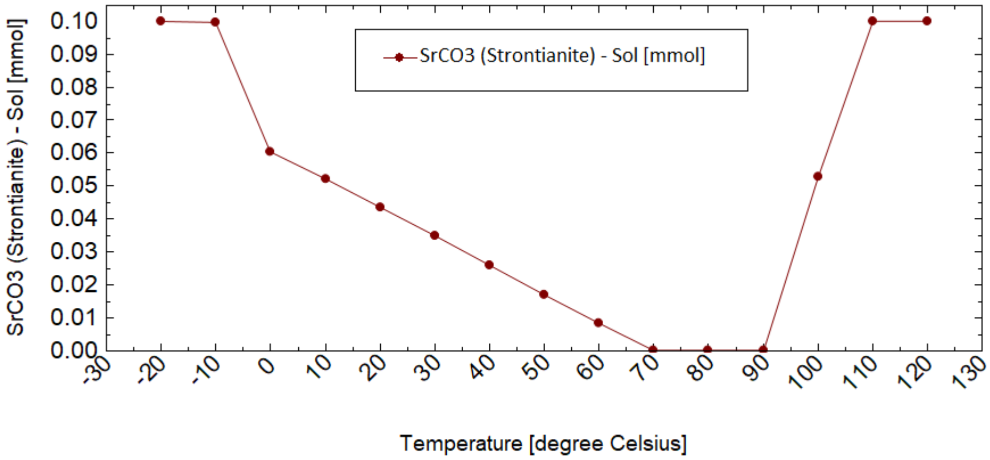
9.2.2. Simulation output: 0.1 mM

Process Conditions

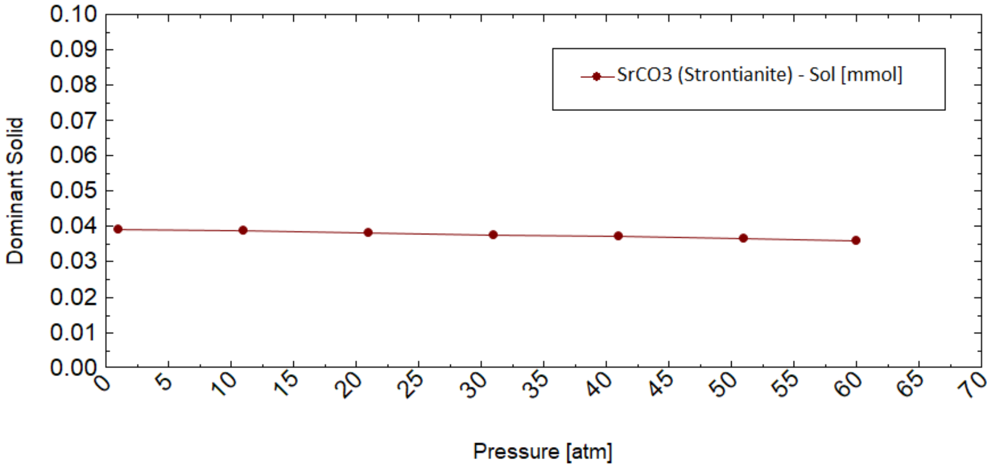
- pH



- Temperature

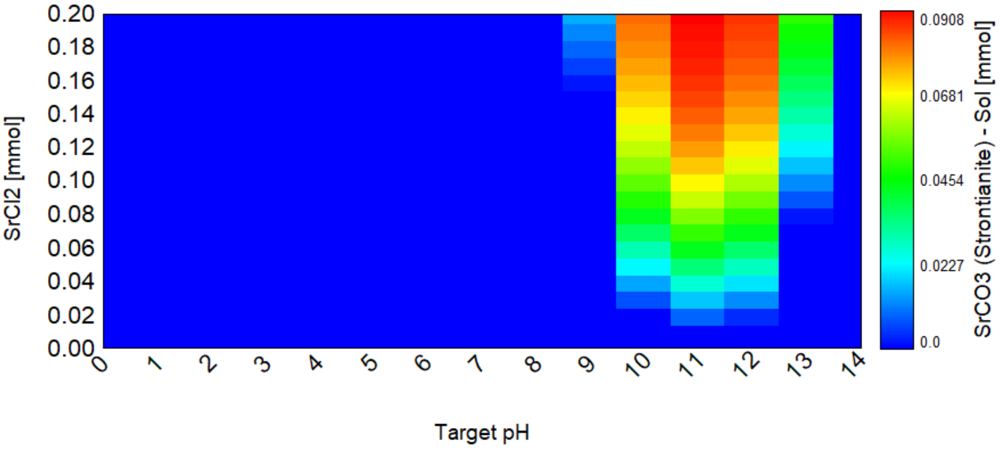


- Pressure

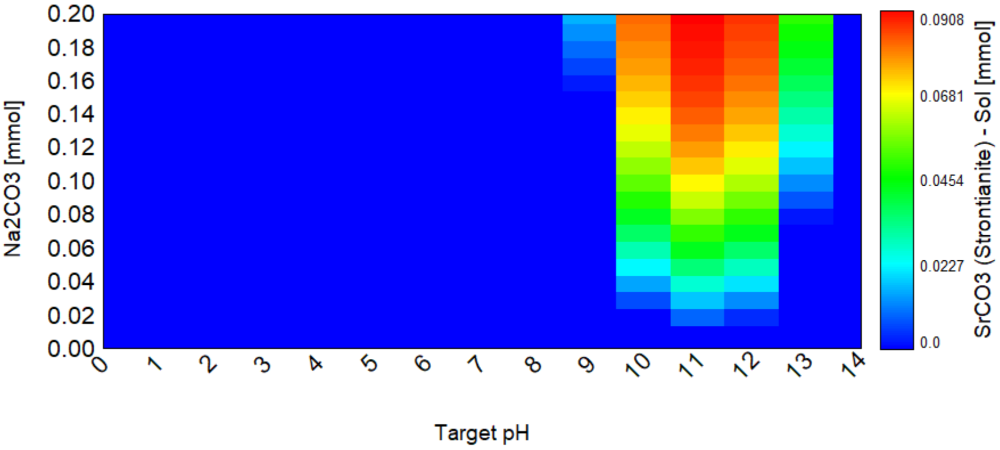


Driving Force

- Strontium concentration

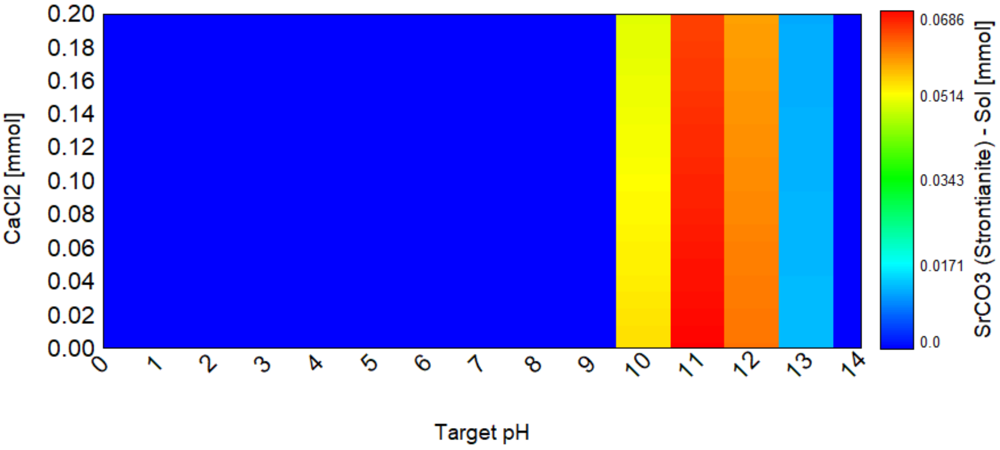


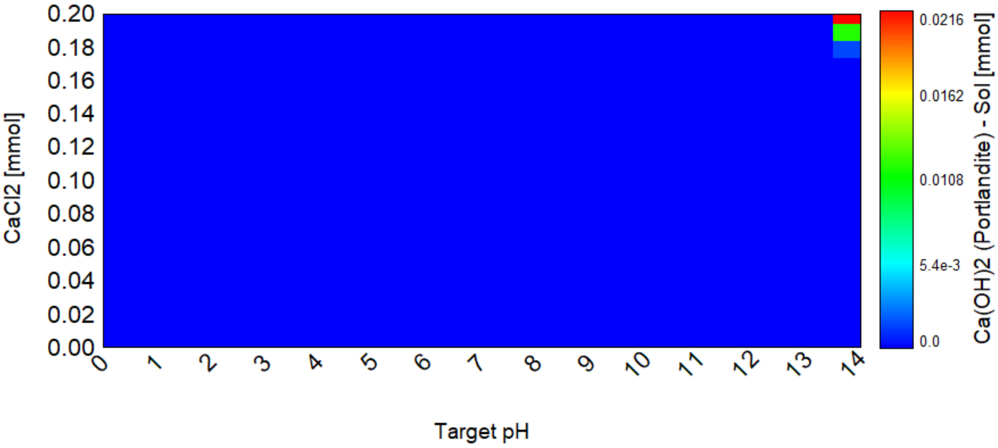
- Inorganic carbon concentration



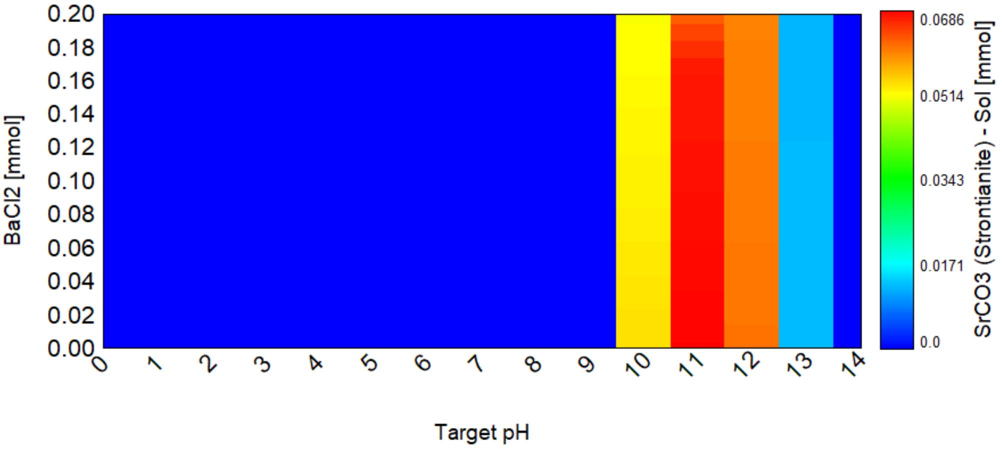
Competitors

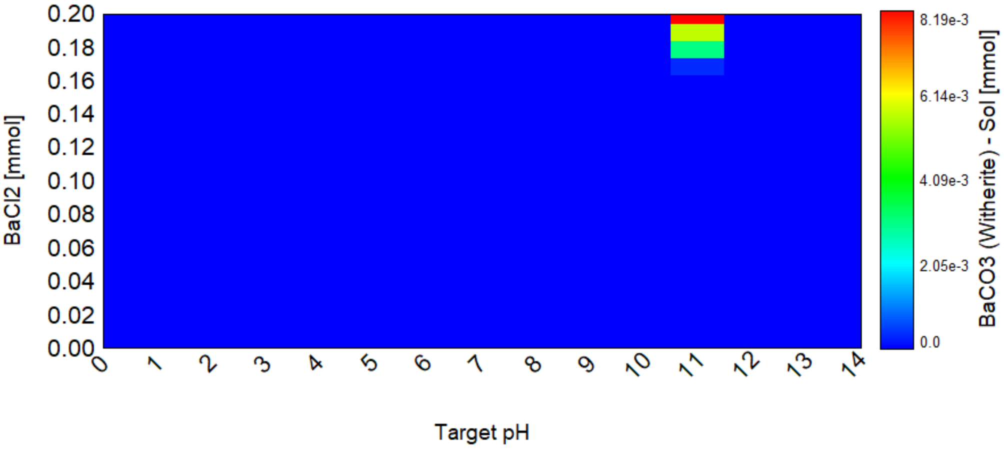
- Calcium concentration



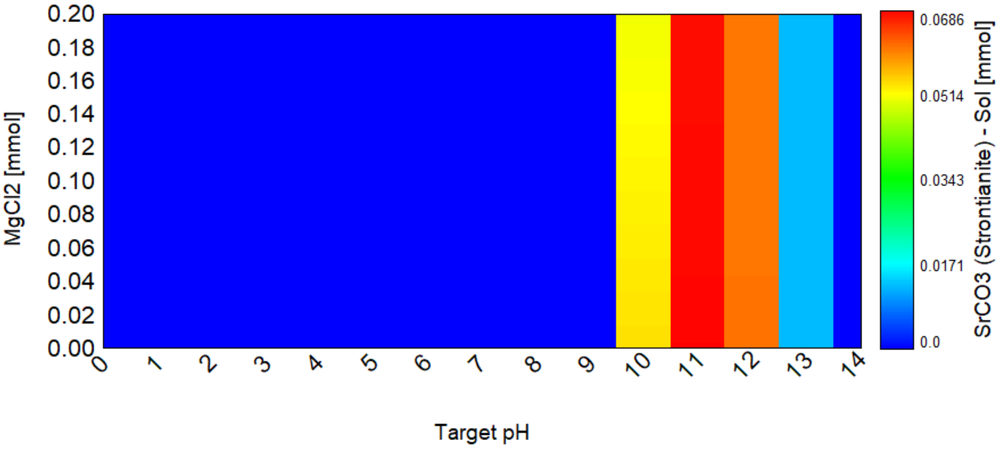

CaCl2 [mmol]
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Target pH
0.0216
0.0162
0.0108
5.4e-3
0.0
Ca(OH)2 (Portlandite) - Sol [mmol]

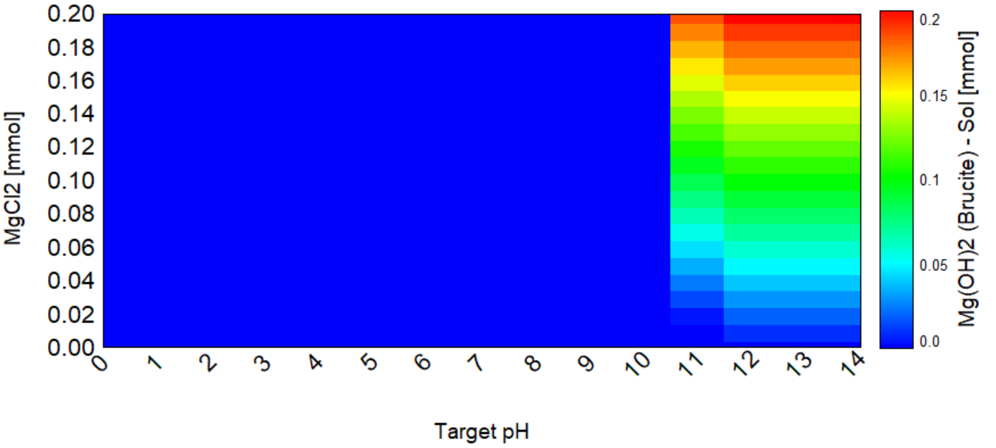
- Barium concentration



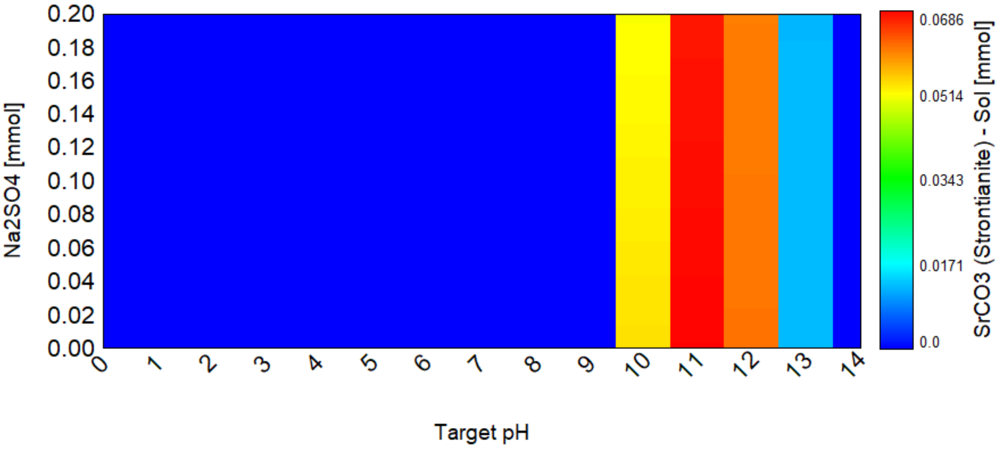


- Magnesium concentration

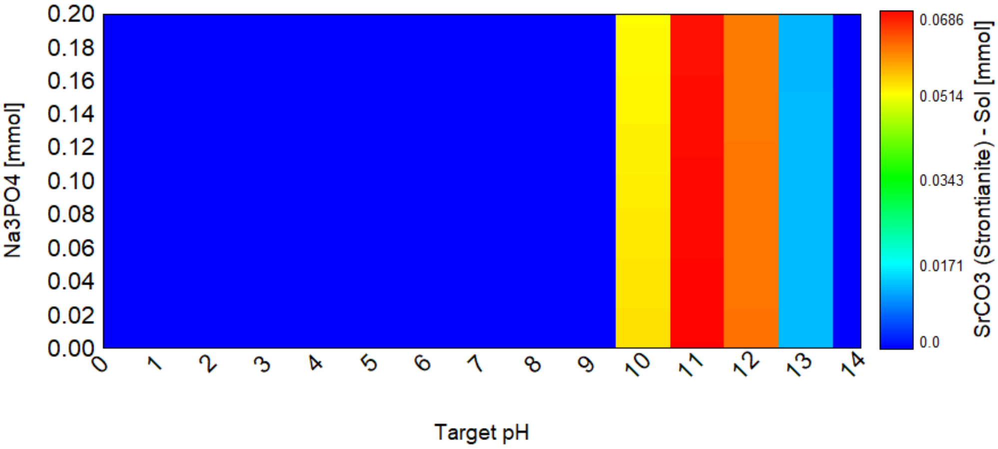




- Inorganic Sulphur concentration

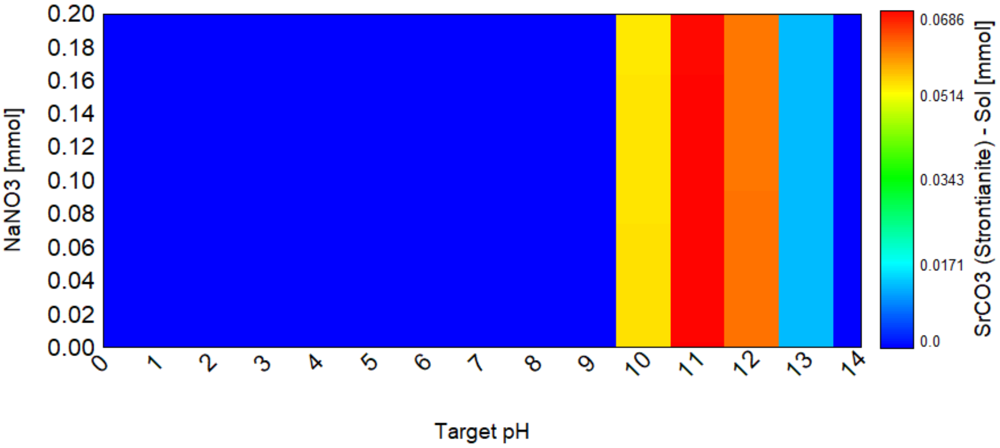


- Inorganic phosphorus concentration

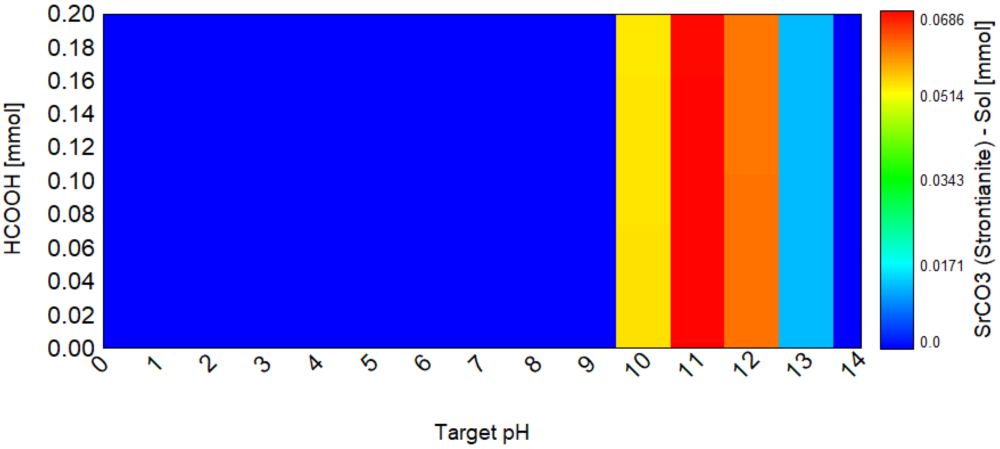


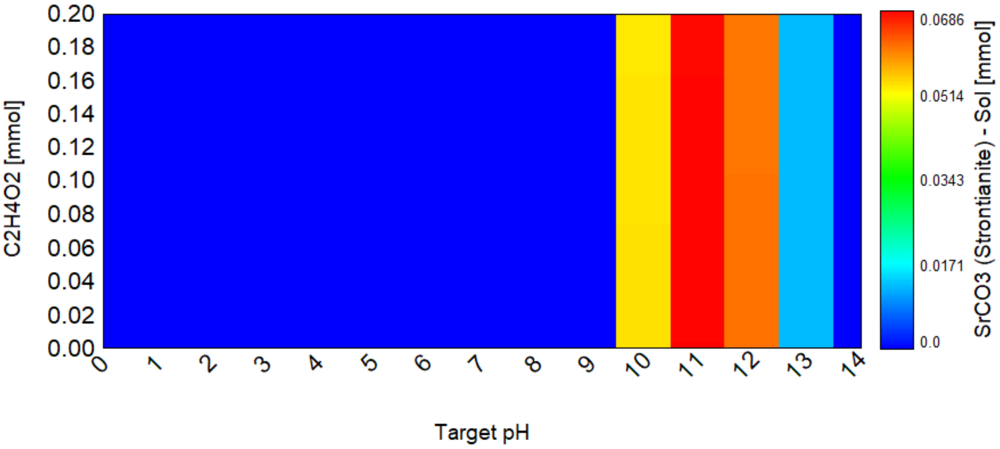
Miscellaneous

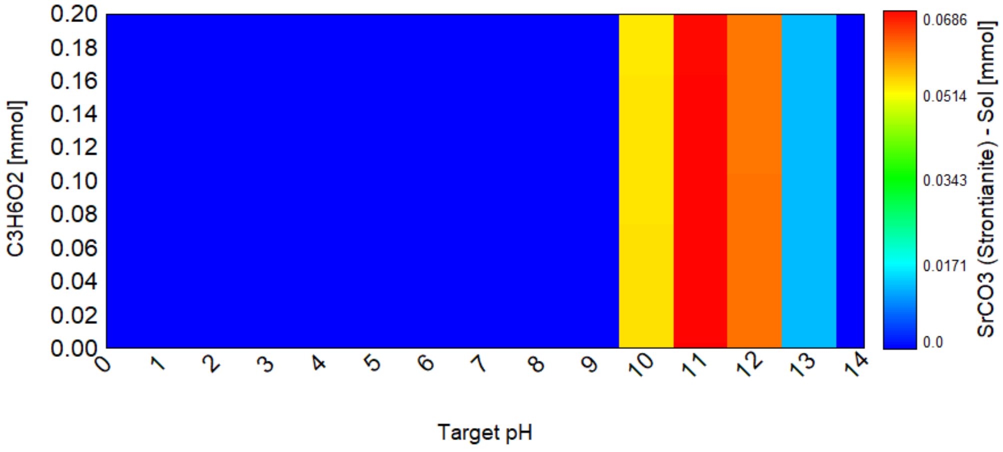
- Ionic Strength



- Natural Organic Matter



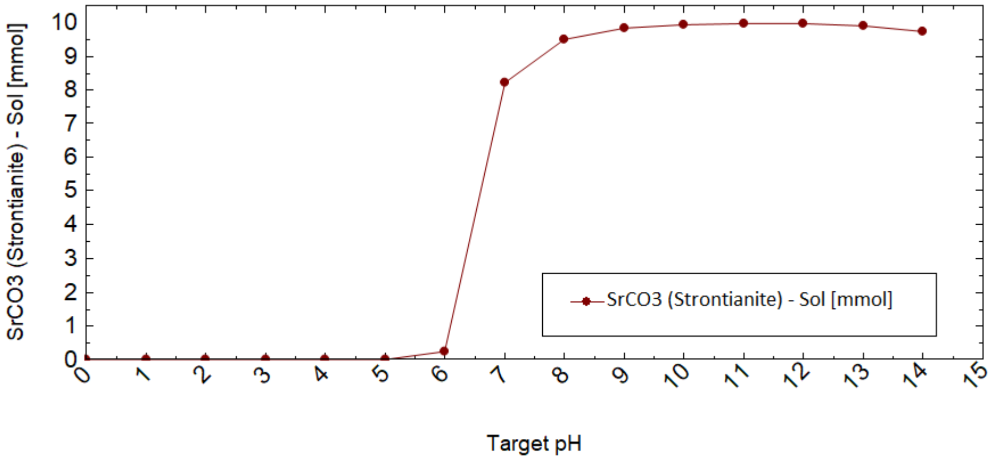




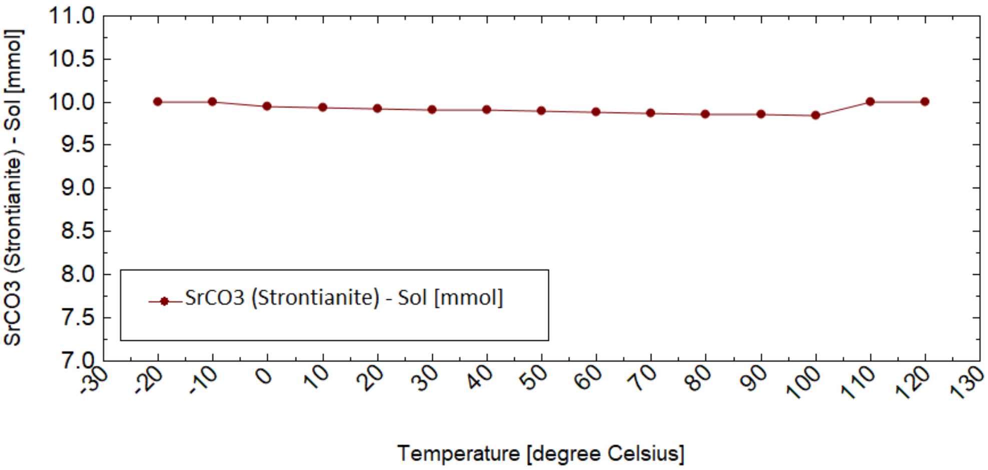
9.2.3. Simulation Output: 10 mM

Process Conditions

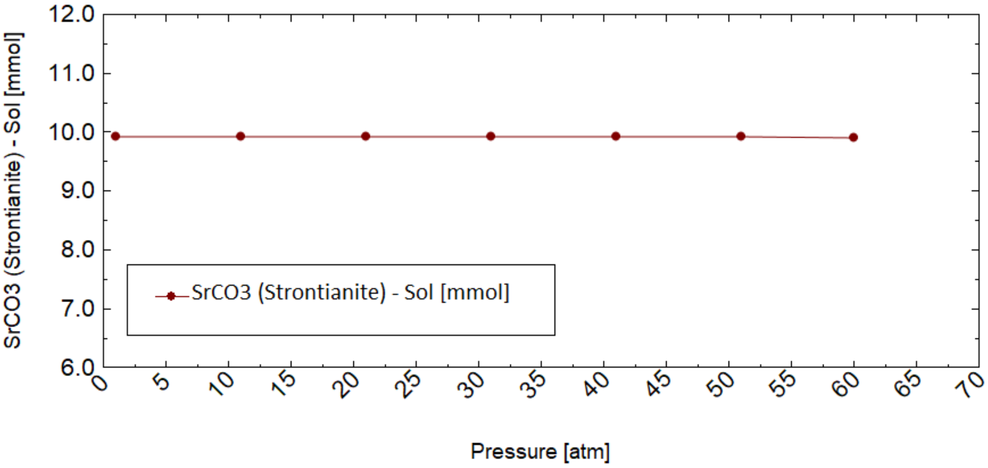
- pH



- Temperature

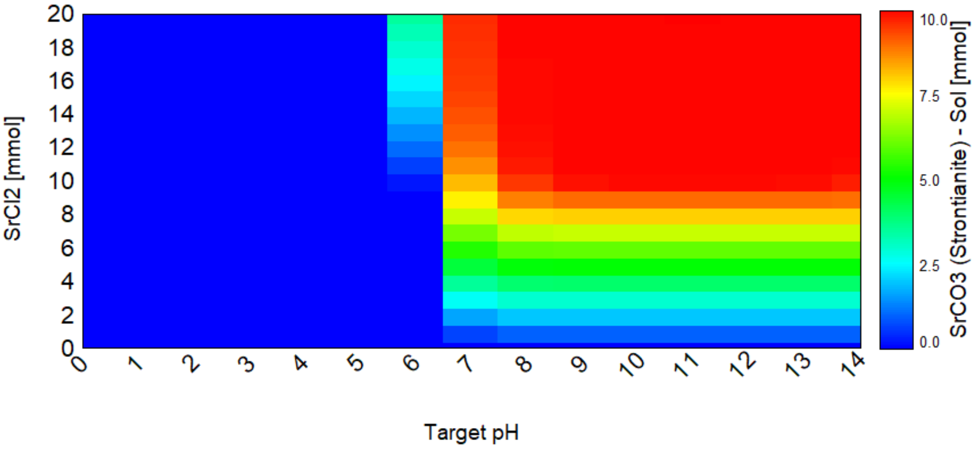

SrCO3 (Strontianite) - Sol [mmol]
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Temperature [degree Celsius]
SrCO3 (Strontianite) - Sol [mmol]

- Pressure

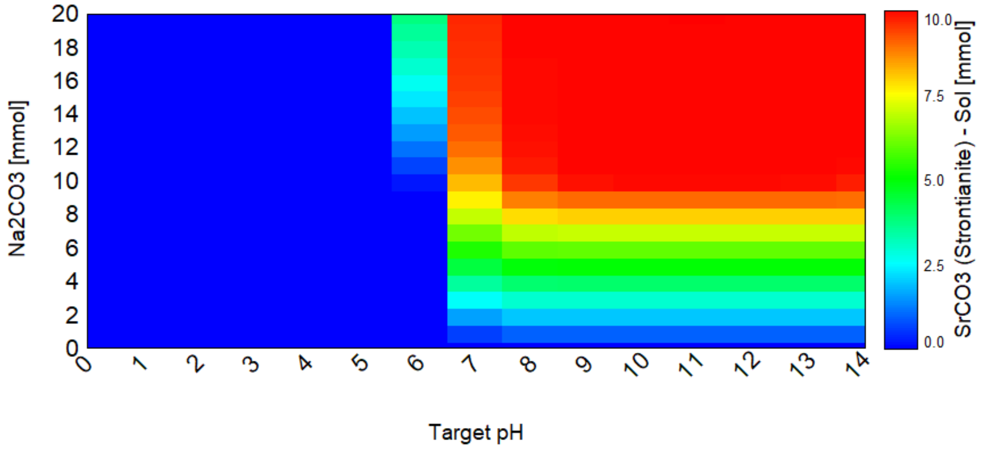


Driving Force

- Strontium concentration

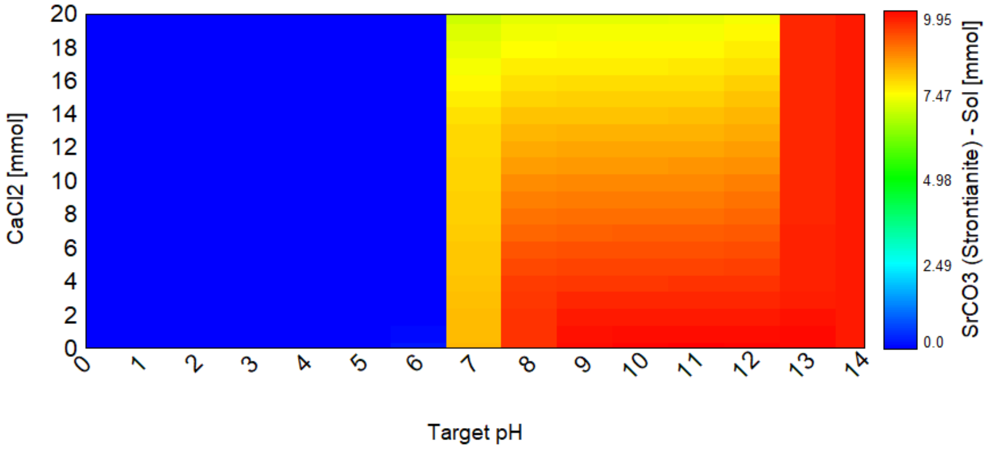


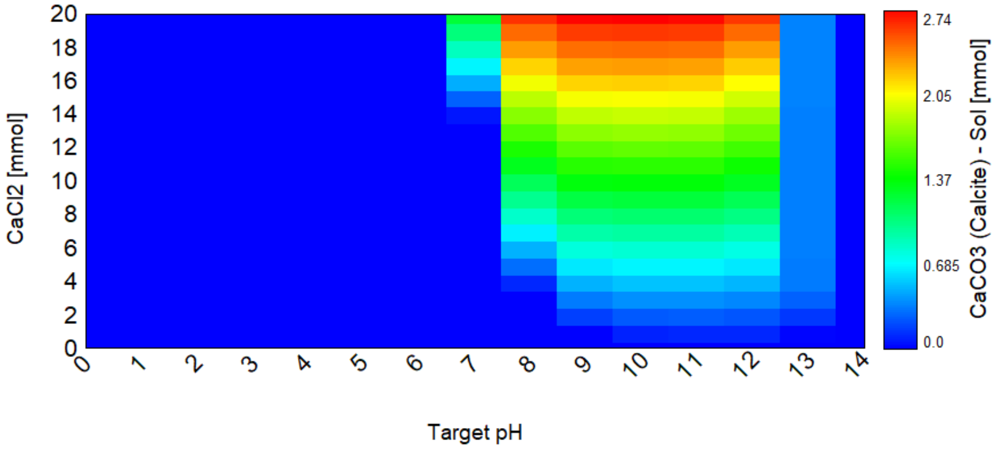
- Inorganic carbon concentration

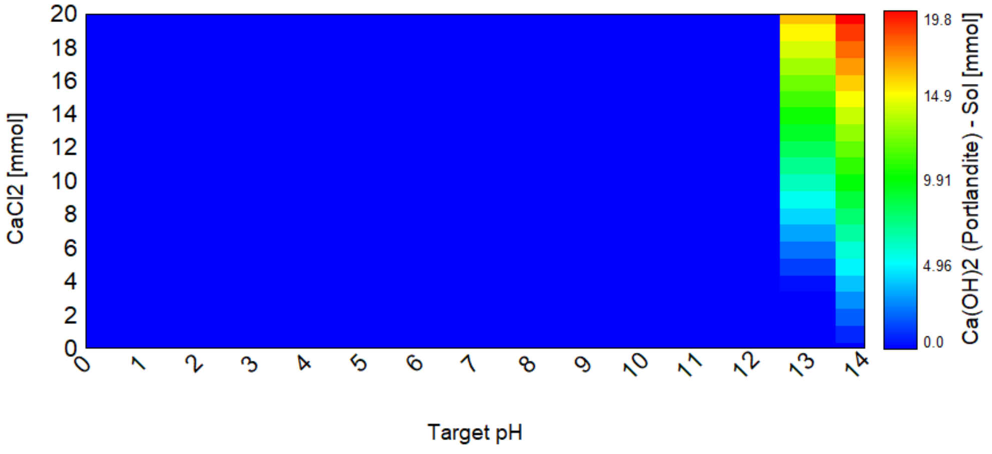


Competitors

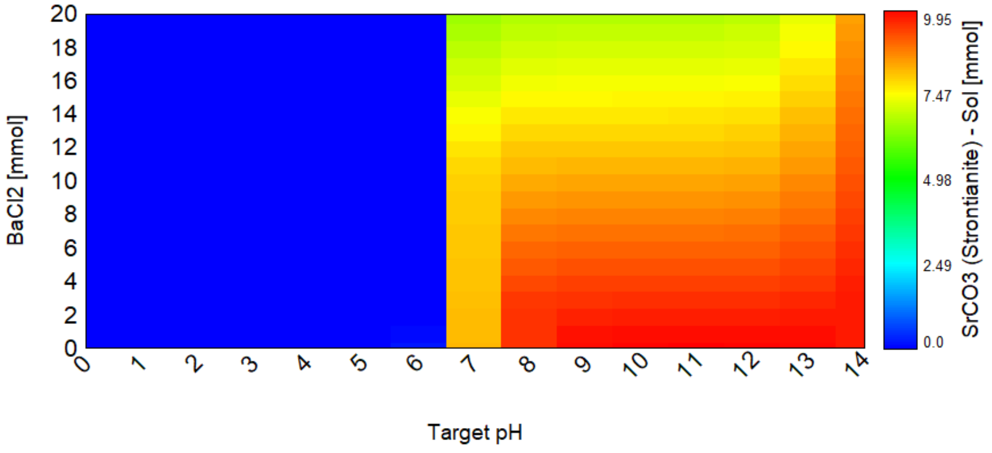
- Calcium concentration

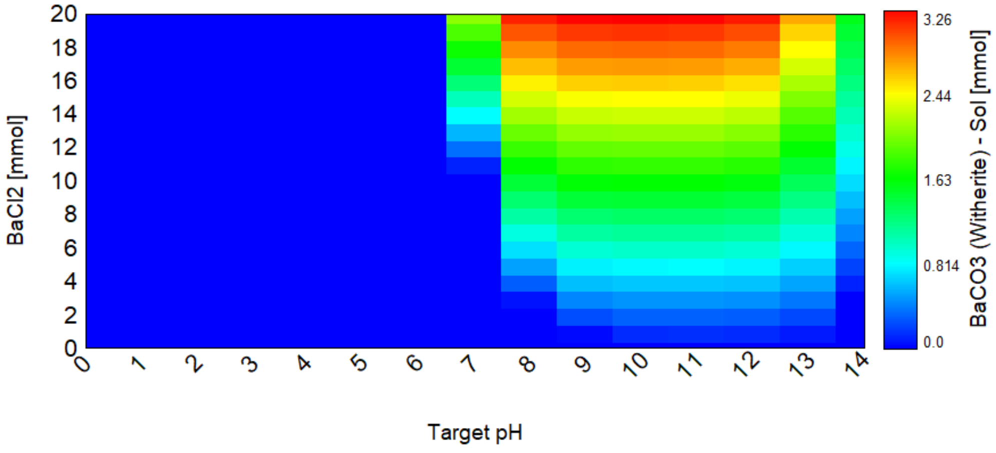




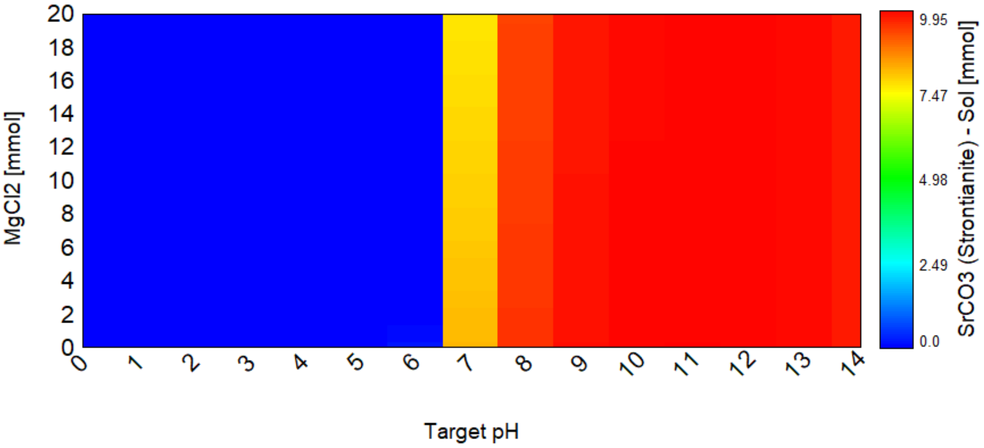


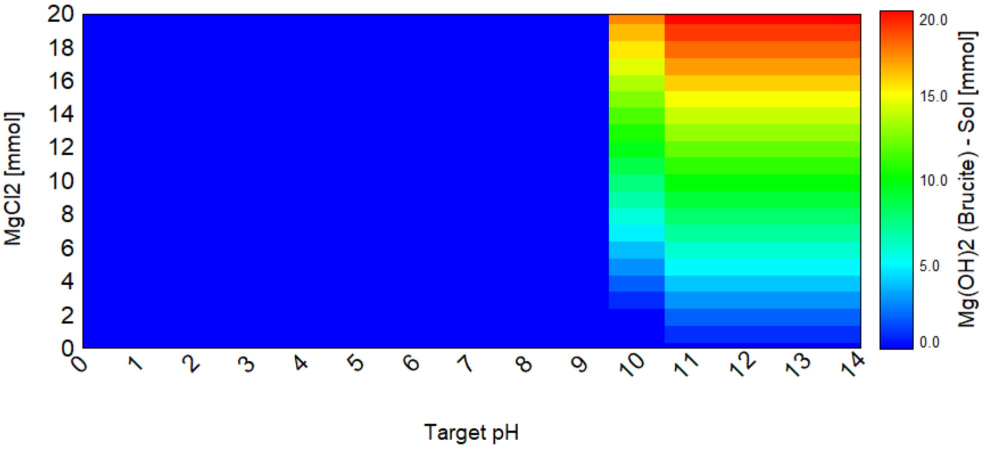
- Barium concentration



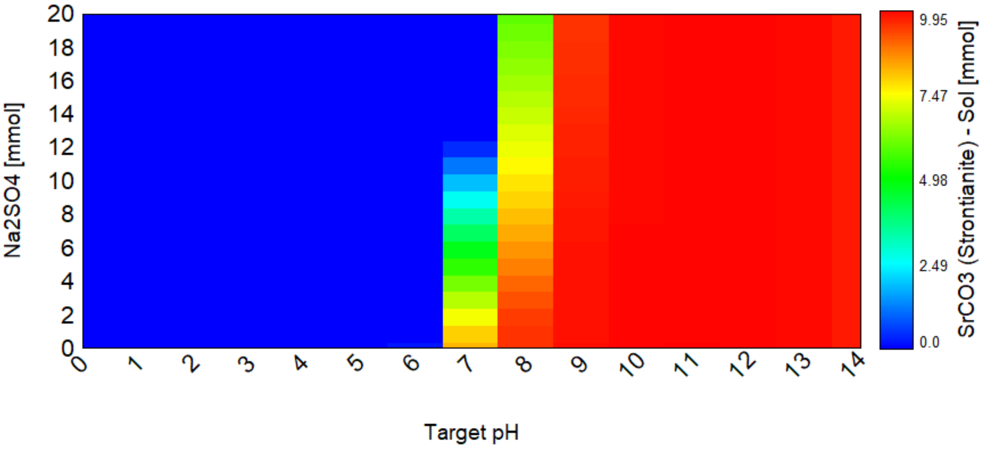


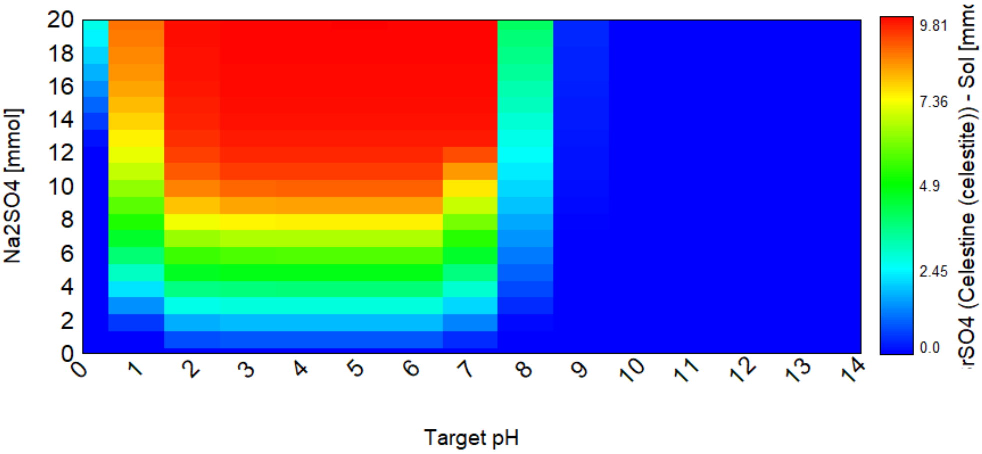
- Magnesium concentration



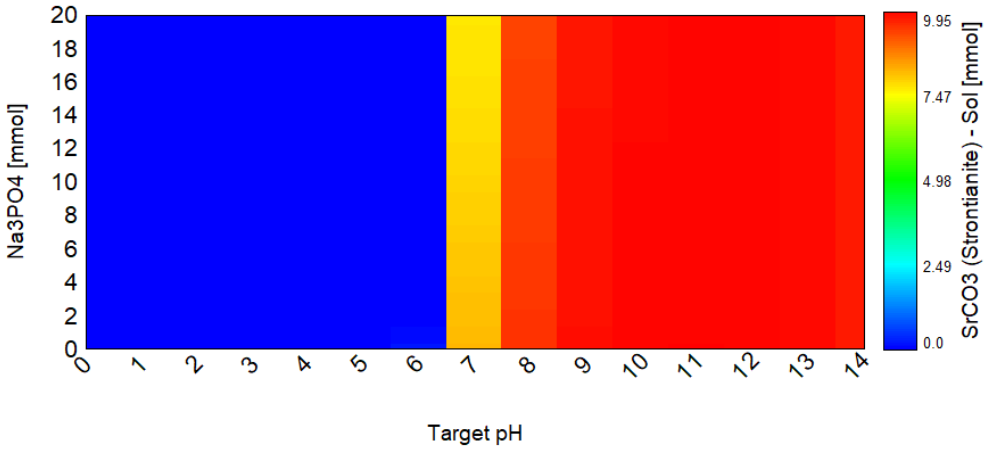


- Inorganic Sulphur concentration



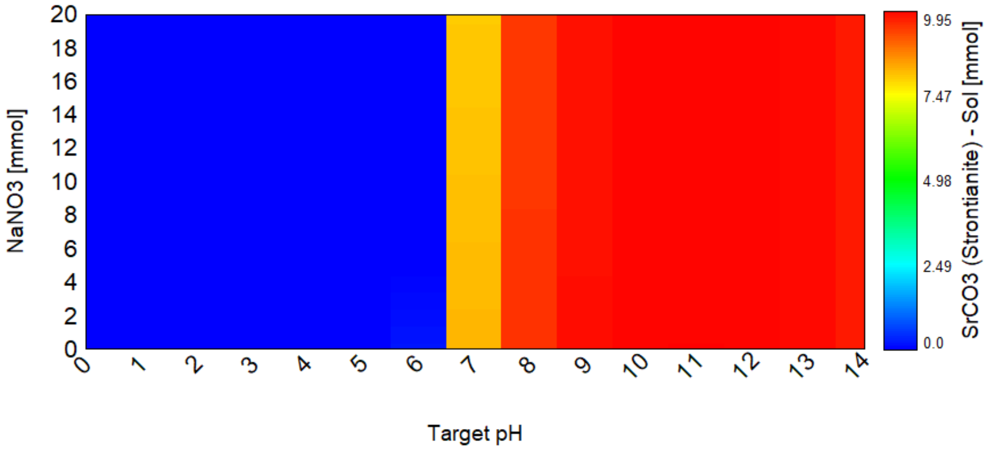

20
18
16
14
12
10
8
6
4
2
0
Na2SO4 [mmol]
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Target pH
9.81
7.36
4.9
2.45
0.0
rSO4 (Celestine (celestite)) - Sol [mmo

- Inorganic Phosphorus concentration

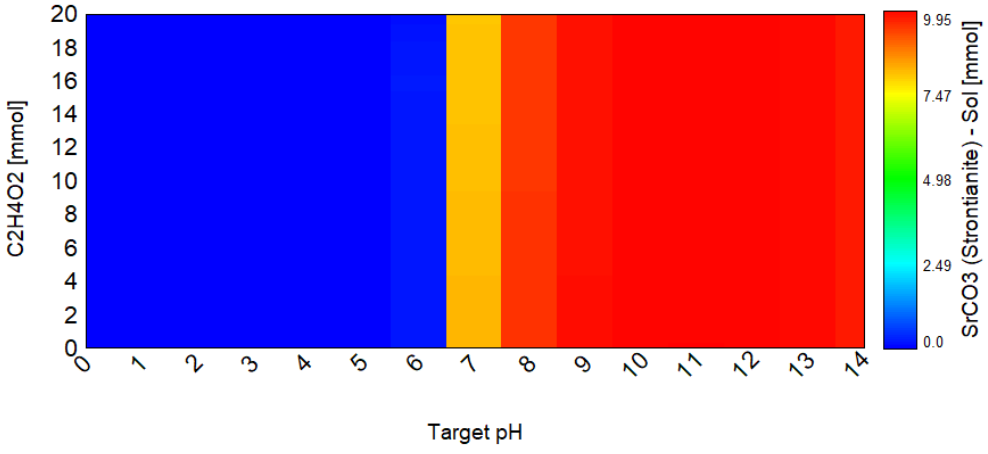


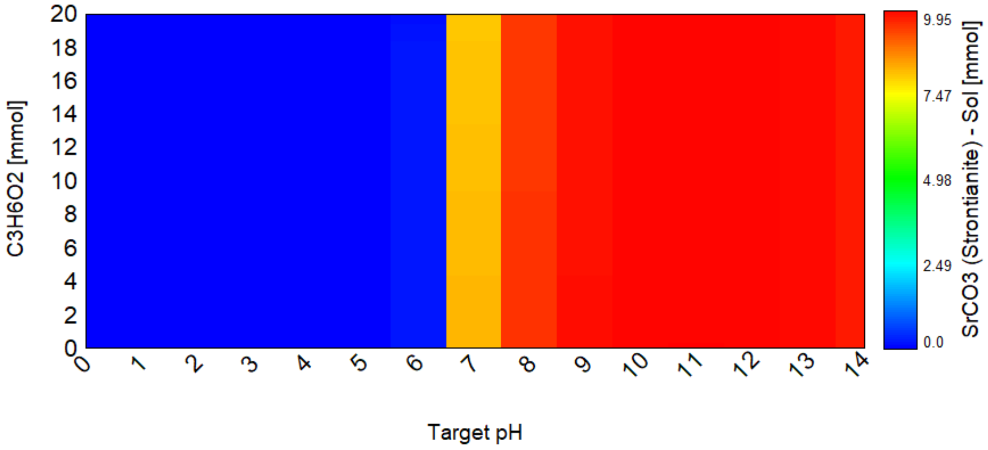
Miscellaneous

- Ionic Strength



- Natural Organic Matter

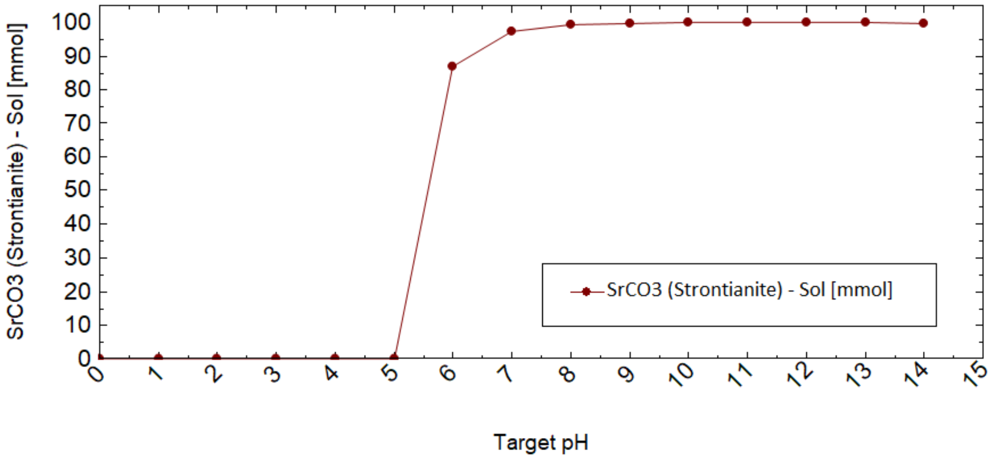




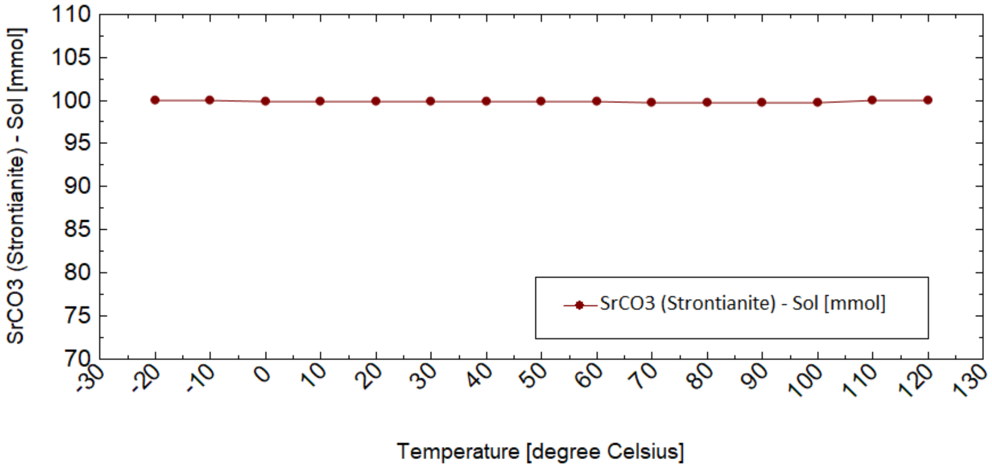
9.2.4. Simulation Output: 100 mM

Process Conditions

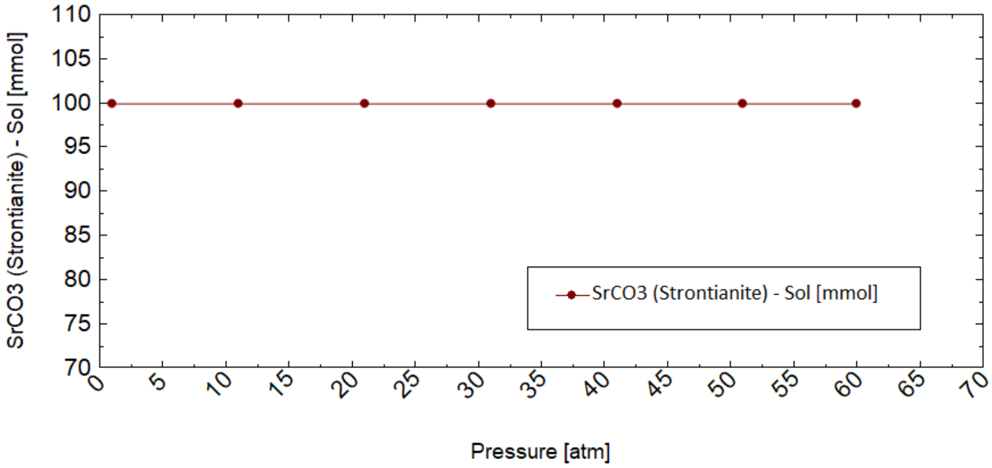
- pH



- Temperature

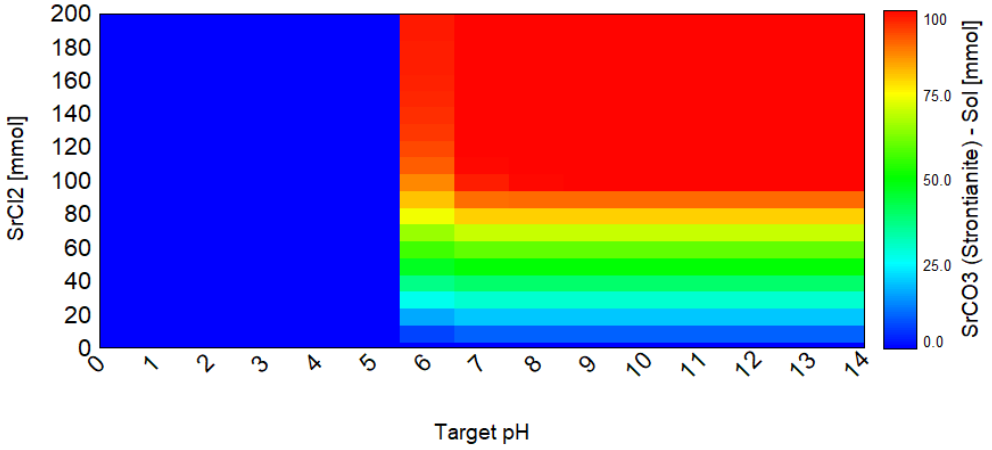


- Pressure

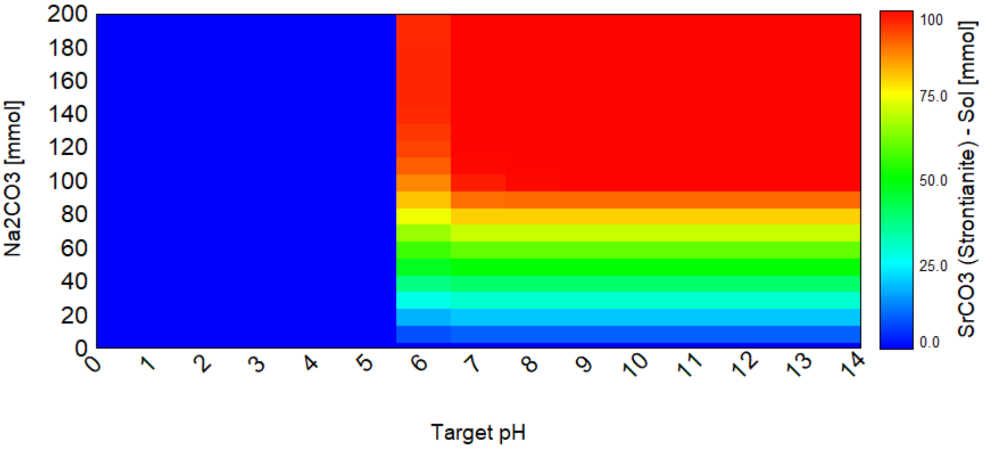


Driving Force

- Strontium concentration

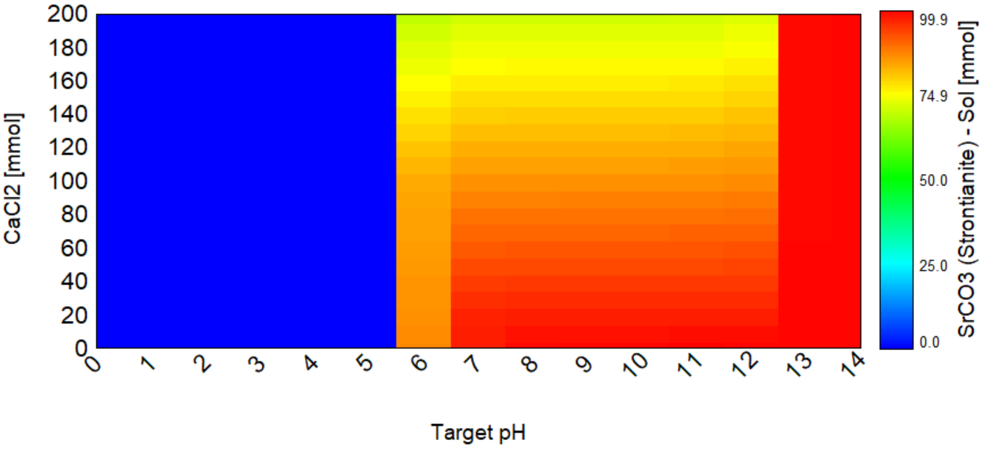


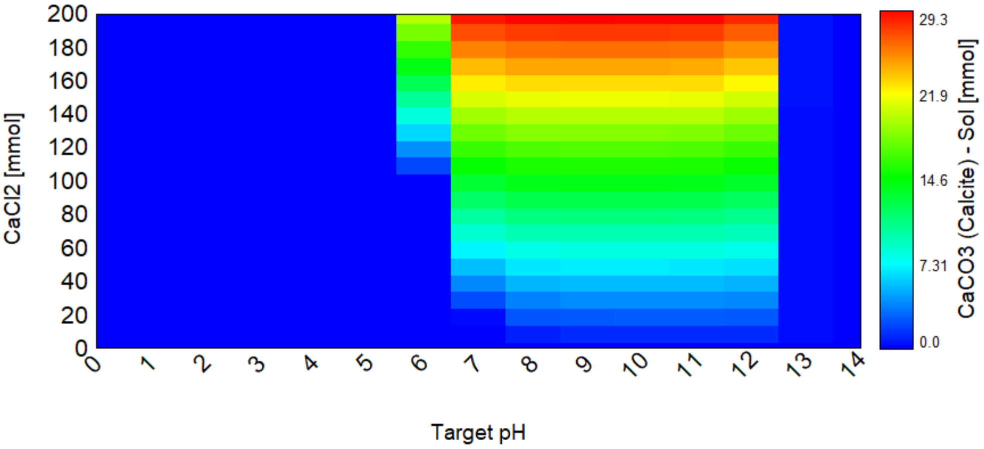
- Inorganic carbon concentration

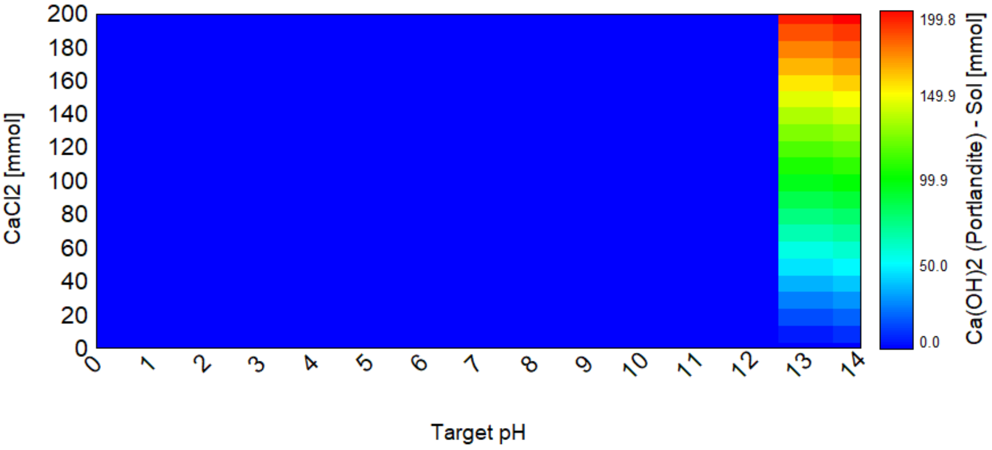


Competitors

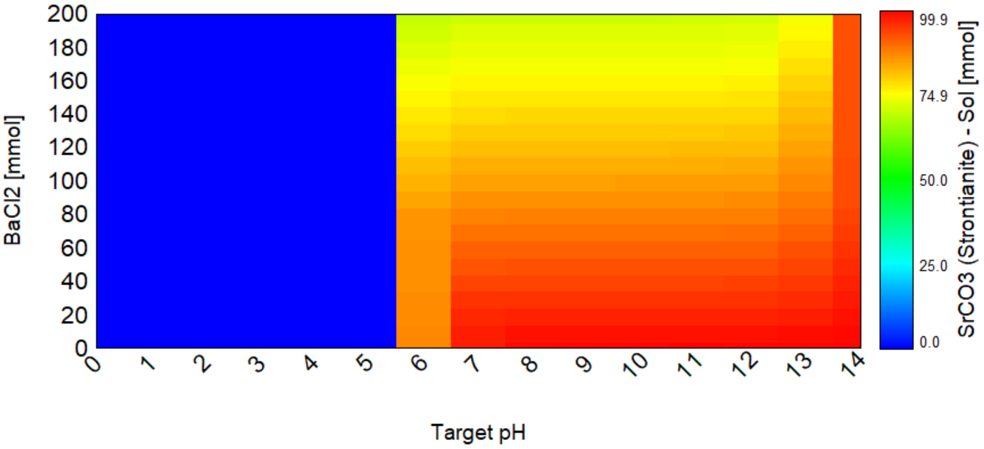
- Calcium concentration

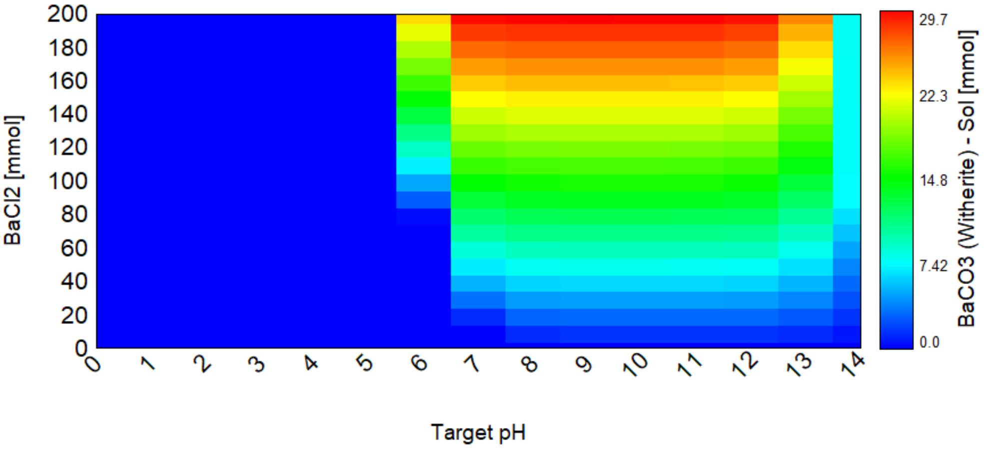


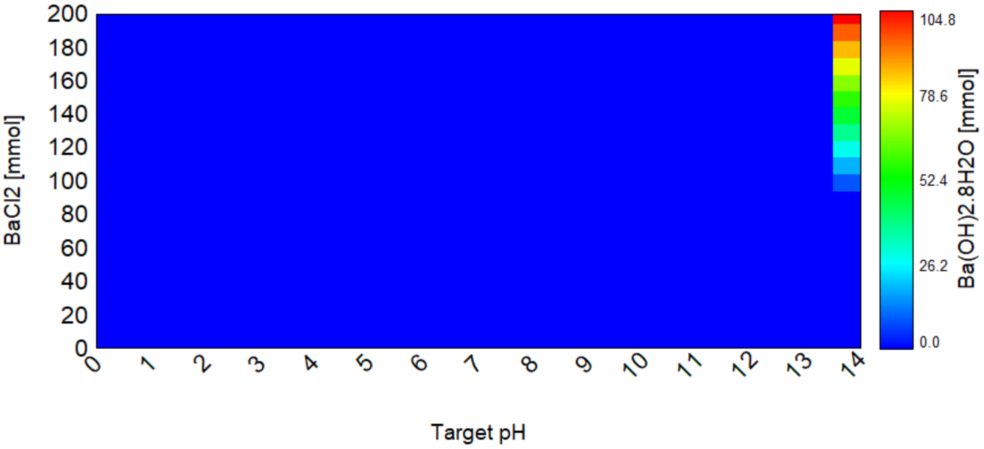



CaCl2 [mmol]
200
180
160
140
120
100
80
60
40
20
0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Target pH
199.8
149.9
99.9
50.0
0.0
Ca(OH)2 (Portlandite) - Sol [mmol]

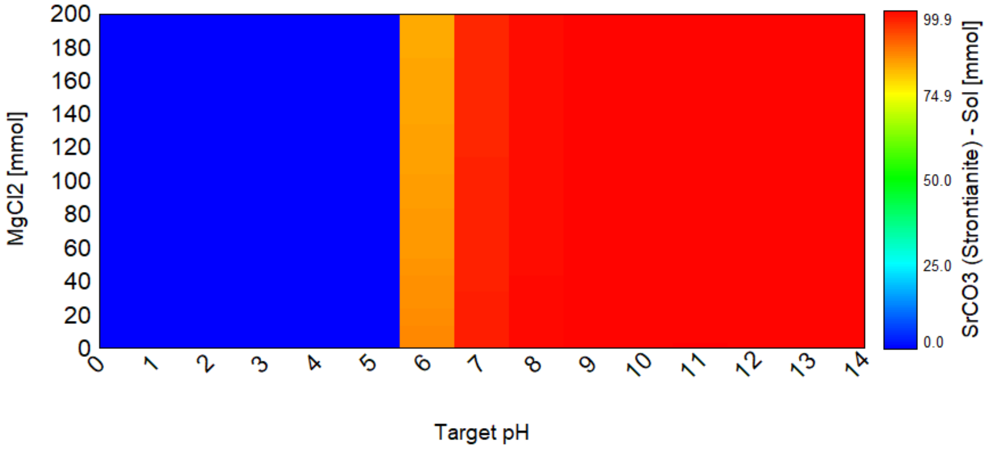
- Barium concentration

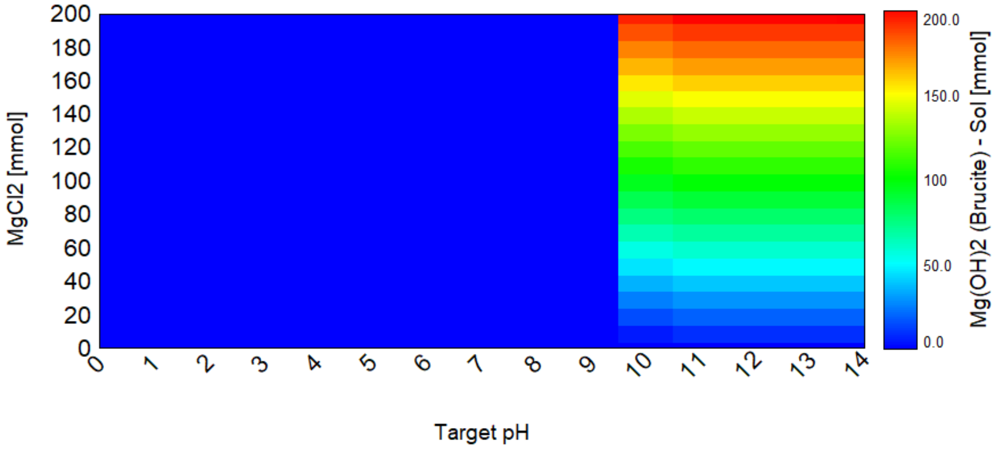




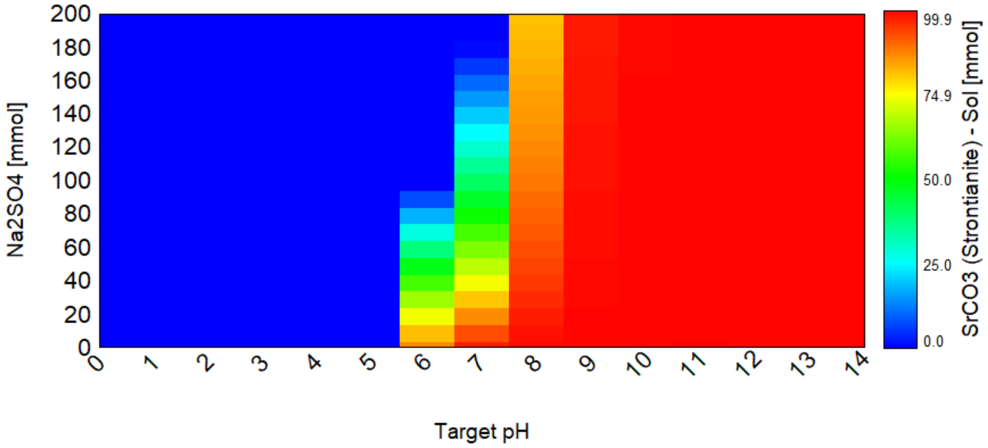


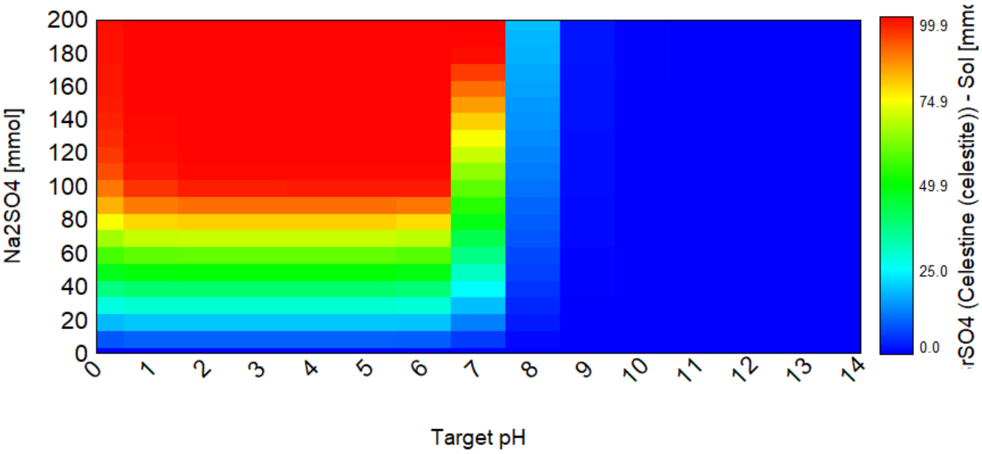
- Magnesium concentration



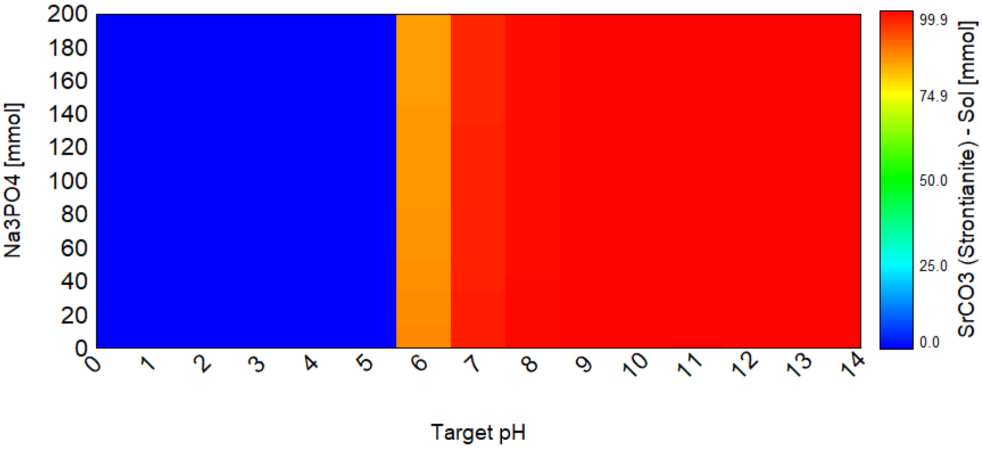


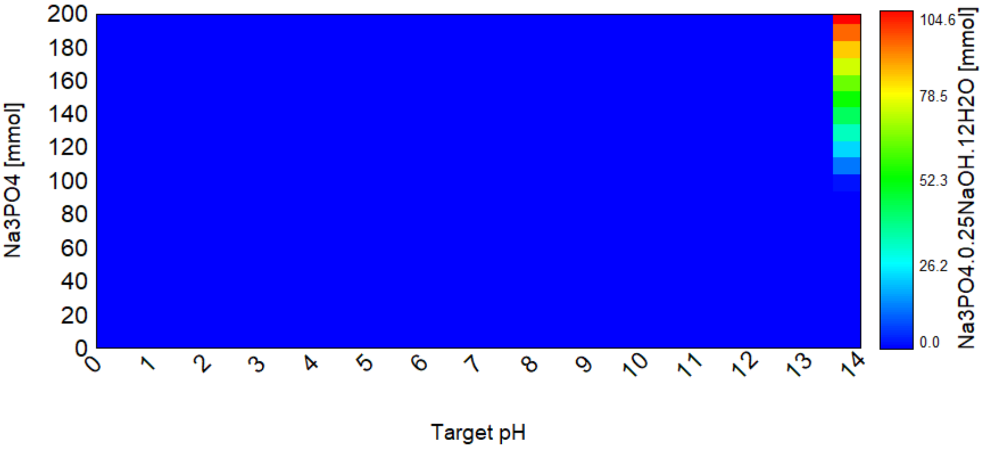
- Inorganic sulphur concentration





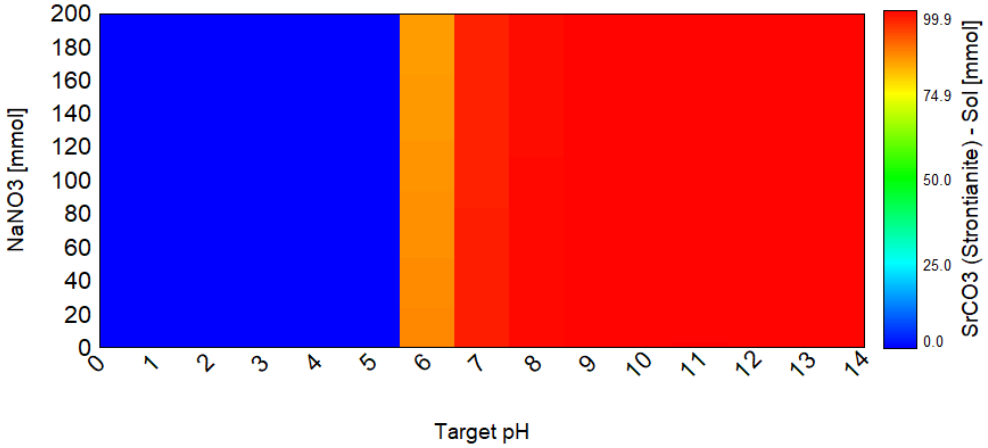
- Inorganic phosphorus concentration



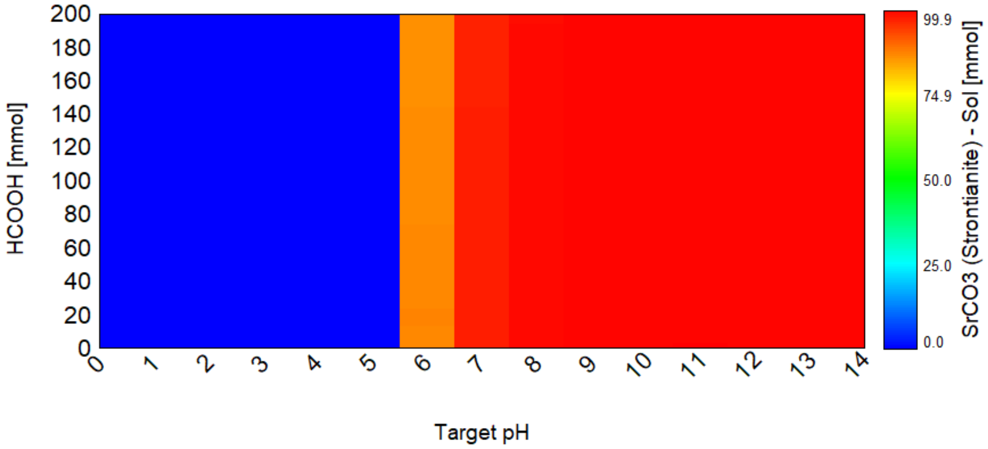


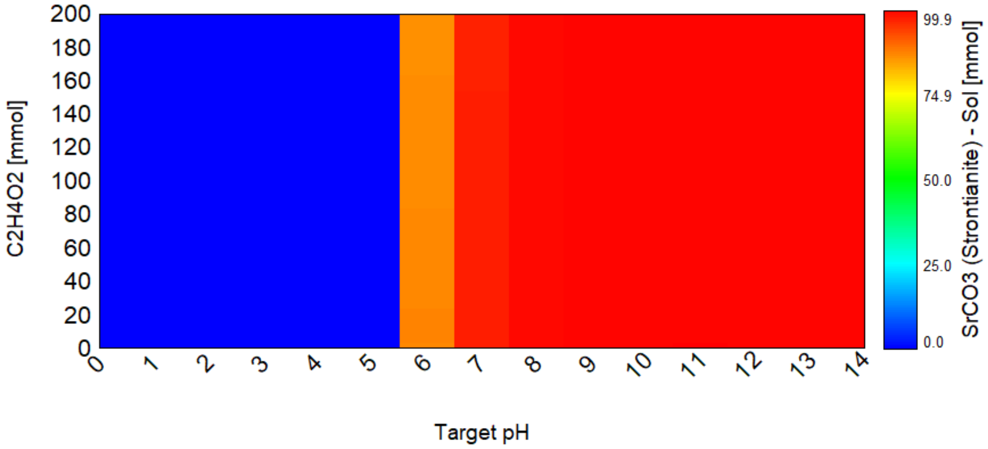
Miscellaneous

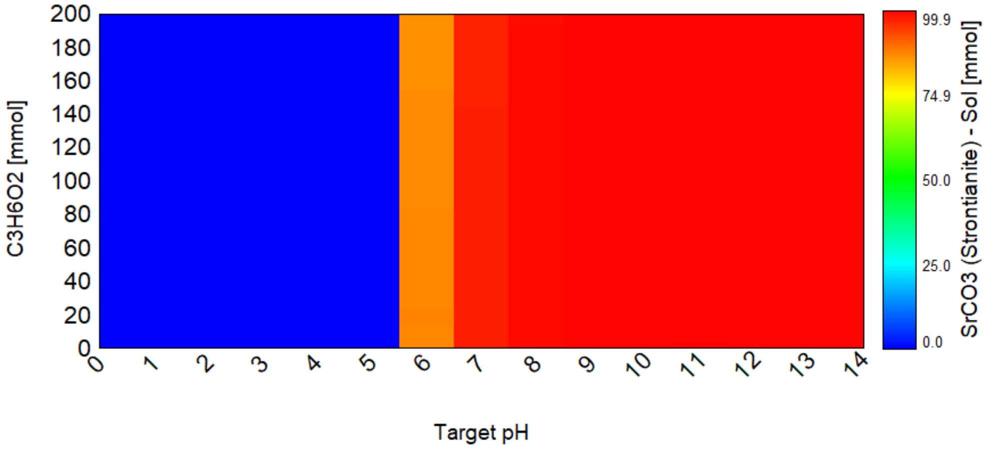
- Ionic Strength



- Natural Organic Matter







9.3. Pre – treatment of Concentrate

9.3.1. Rhine Water Characteristics

Table 35 below represents the quality of Rhine river water from Witteveen+Bos, representative of the quality of feed used for drinking water production at PWN. This data was obtained from: https://www.riwa-rijn.org/publicatie/jaarrapport-2018-de-rijn/

Table 34: Quality of Rhine river water from Witteveen+Bos

Rhine water quality				
Inorganics	Unit	Average	Min	Max
CO_2	mg/l	2.44	2	2.9
HCO_3	mg/l	174	159	196
Cl	mg/l	98.1	44	124
SO_4	mg/l	58.5	37.5	75
Si	mg/l	1.97	0.234	3.23
Br	mg/l	0.2	0.079	0.43
F	mg/l	0.13	0.12	0.16
Nutrients	Unit	Average	Min	Max
NH_4^+	mg/l	0.123	0.07	0.28
NO_2	mg/l	0.0912	0.048	0.151
NO_3	mg/l	9.01	3.64	13.1
Orthophosphate PO_4	mg/l	0.192	0.09	0.27
Total PO_4	mg/l	0.315	0.19	0.6
Metals	Unit	Average	Min	Max
Na	mg/l	46.77	25.1	68.6
K	mg/l	4.46	3.04	6.32
Ca	mg/l	68.5	57.7	76.4
Mg	mg/l	11.2	9.14	12.5
Fe	mg/l	1.09	0.41	2.01
Mn	µg/l	68.1	40	93
Al	µg/l	992	397	1650
Ba	µg/l	80.1	63.9	102
Sr	µg/l	465	329	542
Total	Unit	Average	Min	Max
Salts	mg/l	478.696	343.191	584.338

9.3.2. IMSDesign: Feed to RO

Table 35: Composition of the feed to RO at PWN

Parameter	Units	Feed (to RO)		
		Average	**S.D**	**n**
Cations				
Na^+	*mg/L*	94.9	16.1	12
Ca^{2+}	*mg/L*	56.8	8.57	23
Mg^{2+}	*mg/L*	13.4	1.77	23
Sr^{2+}	*mg/L*	0.405	0.0264	12
Ba^{2+}	*mg/L*	0.0406	0.0032	12
Iron	*µg/L*	0.979	0.701	12
K^+	*mg/L*	?	-	-
Al^{3+}	*mg/L*	?	-	-
Anions				
Cl^-	*mg/L*	169	23.5	23
HCO_3^-	*mg/L*	136	17	12
SO_4^{2-}	*mg/L*	56.96	1.42	1
NO_3^-	*mg/L N*	?	-	-
CO_3^{2-}	*mg/L*	0	0	12
PO_4^{3-}	*mg/L P*	?	-	-
Others				
pH	*-*	7.92	0.111	12
Temperature	*°C*	11.9	5.21	12
Conductivity	*mS/m*	80.9	8.44	45
CO_2	*mg/L*	3.09	0.73	12
DO	*mg/L O_2*	?	-	-
TOC	*mg/L*	2.87	0.247	11
Total hardness	*mmol/L*	1.97	0.242	23
COD	*mg/L O_2*	?	-	-
Silicate	*mg/L Si*	0.823	0.295	12
DCT	*cel/mL*	502	293	4
AOC	*mg/L C*	0.0158	0.0214	3
ATP	*ng/L*	1.46	0.605	4

9.4. Detailed Experimental Procedure

1. Preparation of stock solutions

1.1. Desired concentration (in mM) of the stock solution and the required volume (in mL) was decided.

1.2. Required amount of salt was calculated using the following equation

1.3. Ultrapure water was measured using a measuring cylinder and the calculated amount of salt was measured using a weighing scale.

1.4. The measured salt was dissolved in the ultrapure water with the help of a magnetic stirrer. The solution was stored in 250 ml glass bottles

2. Preparing experimental solutions

2.1. Each experimental solution/trial was based on the created table of designs. Experiments were carried out in 250 mL glass beakers.

2.2. Depending on the desired concentration of the component, the required amount of stock solution to be added was calculated by:

2.3. The volume of ultrapure water to be added was calculated by subtracting the summation of all required stock solution volumes from the target volume of the experiment

2.4. The required amount of ultrapure water was measured using a measuring cylinder (to the nearest whole number) and adjusted with a micropipette.

2.5. The pH of the ultrapure water was adjusted to the desired value using a NaOH solution and a micropipette

2.6. All the prepared stock solutions were pipetted in according to the calculated volume with the help of a micropipette. The stock solutions were added while the set up was being continuously mixed by a magnetic stirrer. Each stock solution was also mixed with a magnetic stirrer prior to being added.

2.7. After each experiment, the glass bottles were washed with regular soap, rinsed with concentrated HNO_3 and then rinsed with demiwater to remove residual HNO_3. The bottles were then left partially open to dry after which they ready to be used again.

3. Collection and preparation of samples

3.1. Once each stock solution was added, the solution was kept mixed over a magnetic stirrer for a minute.

3.2. The initial samples were collected at this stage. The experimental solution was left undisturbed till it was time to collect the final samples.

3.3. Final samples were to be collected based on the availability of lab schedule. The time between the collection of initial and final samples was either 18 hours or 42 hours.

3.4. Each sample was filtered over a 0.45 um filter and acidified 1% v/v with 69% HNO_3[25]. The sample was diluted to the measuring range of ICP-MS with 1% HNO_3. Further 69% HNO_3 was added to the final sample to maintain the required 1% v/v.

3.5. The labelled samples were placed in a refrigerator (3 - 4 C) till analysis could be carried out.

4. Analysis

4.1. Analysis of the samples was carried out using an ICP – MS available in the lab. The samples were measured by the lab technicians.

4.2. Apart from the regular standards used to calibrate the device, internal standards were also prepared in an identical fashion to the samples and also analysed.

4.3. Samples would be measured in groups at the end of the week. Therefore, the time between collection of sampled varied from a few hours to 4 days.

4.4. The results from the ICP – MS were corrected for dilution. These were the final results and used for further calculations, analysis and conclusions

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[25] To reduce pH to arrest any further reaction in the sample

9.5. Aqueous concentration: Experiments vs OLI

Mg

Table 36: Comparison of experimentally observed aqueous concentration of Mg with OLI predicted values

StdOrder	ICP - MS	OLI	Ratio	StdOrder	ICP - MS	OLI	Ratio
	mM	mM			mM	mM	
1	1.037	1.000	1.037	**28**	0.036	0.000	1057.070
2	0.004	0.00003	127.822	**29**	1.095	1.000	1.095
3	1.016	1.000	1.016	**30**	0.018	0.00003	543.899
4	0.030	0.00003	891.443	**31**	1.124	1.000	1.124
5	1.077	1.000	1.077	**32**	0.026	0.00003	756.536
6	0.023	0.00003	679.404	**33**	0.227	0.048	4.725
7	1.028	1.000	1.028	**34**	0.173	0.053	3.289
8	0.009	0.00003	249.853	**35**	0.249	0.053	4.682
9	0.938	0.572	1.641	**36**	0.148	0.055	2.696
10	0.647	0.577	1.122	**37**	1.769	1.291	1.370
11	1.032	0.567	1.818	**38**	1.195	1.299	0.920
12	0.870	0.573	1.518	**39**	1.809	1.293	1.399
13	1.082	0.576	1.877	**40**	1.021	1.300	0.785
14	0.650	0.581	1.119	**41**	0.289	0.250	1.156
15	1.042	0.572	1.823	**42**	0.006	0.00003	188.895
16	0.865	0.578	1.497	**43**	0.318	0.250	1.273
17	0.302	0.049	6.161	**44**	0.006	0.00003	172.669
18	0.222	0.048	4.643	**45**	1.858	1.750	1.062
19	0.275	0.055	4.992	**46**	0.055	0.00003	1595.723
20	0.190	0.054	3.505	**47**	2.160	1.750	1.234
21	1.646	1.297	1.269	**48**	0.016	0.00003	463.763
22	1.514	1.260	1.201	**49**	1.055	0.575	1.835
23	1.530	1.301	1.176	**50**	0.403	0.575	0.701
24	0.984	1.299	0.758	**51**	1.029	0.575	1.789
25	1.124	1.000	1.124	**52**	1.096	0.575	1.906
26	0.040	0.00003	1206.795	**53**	0.434	0.575	0.755
27	1.114	1.000	1.114	**54**	0.444	0.575	0.772

S

Table 37: Comparison of experimentally observed aqueous concentration of S with OLI predicted values

StdOrder	**ICP - MS**	**OLI**	**Ratio**	**StdOrder**	**ICP - MS**	**OLI**	**Ratio**
	mM	mM			mM	mM	
1	3.54855	0.950	3.734	**28**	8.817592	0.209	42.162
2	10.6424	0.952	11.179	**29**	3.18107	1.700	1.871
3	3.44995	0.950	3.631	**30**	10.11938	1.701	5.949
4	11.6409	0.952	12.228	**31**	3.441291	1.700	2.024
5	6.78498	0.950	7.140	**32**	11.36695	1.701	6.682
6	11.1658	0.952	11.729	**33**	8.413382	0.201	41.839
7	10.4295	0.950	10.975	**34**	0	0.950	0.000
8	5.3261	0.952	5.594	**35**	4.668676	1.700	2.746
9	2.30865	0.201	11.474	**36**	0	1.700	0.000
10	0	0.201	0.000	**37**	0.520589	0.201	2.586
11	0	0.201	0.000	**38**	0	0.950	0.000
12	0.59882	0.201	2.975	**39**	1.35491	1.700	0.797
13	0	1.700	0.000	**40**	0	1.700	0.000
14	0	1.634	0.000	**41**	6.917486	0.950	7.280
15	1.12008	1.700	0.659	**42**	12.72665	0.952	13.368
16	3.58138	1.700	2.106	**43**	4.037998	0.950	4.249
17	0	0.950	0.000	**44**	9.015378	0.952	9.470
18	3.42461	0.950	3.604	**45**	0.900331	0.950	0.947
19	3.41831	0.950	3.597	**46**	12.44159	0.952	13.069
20	0	0.950	0.000	**47**	5.497334	0.950	5.785
21	0.43899	0.950	0.462	**48**	10.38824	0.952	10.912
22	4.28579	0.950	4.510	**49**	2.384413	0.950	2.509
23	1.30136	0.950	1.369	**50**	0.674555	0.950	0.710
24	0	0.950	0.000	**51**	4.423714	0.950	4.655
25	2.06096	0.201	10.251	**52**	4.149322	0.950	4.366
26	9.21108	0.209	44.094	**53**	0	0.950	0.000
27	0	0.201	0.000	**54**	0	0.950	0.000

Ca

Table 38: Comparison of experimentally observed aqueous concentration of Ca with OLI predicted values

StdOrder	ICP - MS	OLI	Ratio	StdOrder	ICP - MS	OLI	Ratio
	mM	mM			mM	mM	
1	0	0.166	0.000	**28**	2.424986	1.625	1.493
2	1.947153	0.250	7.789	**29**	2.372416	0.250	9.490
3	1.542545	0.250	6.170	**30**	2.514554	0.250	10.058
4	2.861248	0.250	11.445	**31**	3.092183	1.570	1.969
5	3.43704	1.349	2.549	**32**	2.489945	1.626	1.531
6	1.844887	1.406	1.312	**33**	0	0.669	0.000
7	2.776506	1.750	1.587	**34**	0.150793	1.000	0.151
8	1.064117	1.750	0.608	**35**	0	0.679	0.000
9	0	0.890	0.000	**36**	0.235209	1.000	0.235
10	0.707964	1.000	0.708	**37**	2.698817	0.688	3.921
11	2.025248	0.473	4.286	**38**	0.518833	1.000	0.519
12	2.849401	0.890	3.201	**39**	1.794363	0.700	2.564
13	2.219465	0.901	2.463	**40**	0.215897	1.000	0.216
14	0.3935	1.000	0.394	**41**	0	1.000	0.000
15	0.957401	0.484	1.978	**42**	2.188662	1.000	2.189
16	2.128193	0.901	2.361	**43**	2.844057	0.709	4.011
17	2.362518	0.250	9.450	**44**	2.091489	0.770	2.718
18	2.492956	0.105	23.774	**45**	2.820782	1.000	2.821
19	3.481381	1.750	1.989	**46**	2.684253	1.000	2.684
20	0.12298	1.320	0.093	**47**	2.40257	0.723	3.324
21	1.253151	0.250	5.013	**48**	2.089553	0.769	2.719
22	0.13211	0.161	0.820	**49**	2.206343	0.896	2.462
23	3.55903	1.750	2.034	**50**	2.007643	0.896	2.240
24	0.462024	1.329	0.348	**51**	0	0.896	0.000
25	0	0.250	0.000	**52**	0	0.896	0.000
26	3.088814	0.250	12.355	**53**	0.055706	0.896	0.062
27	4.478971	1.553	2.884	**54**	0.802747	0.896	0.896

Sr

Table 39: Comparison of experimentally observed aqueous concentration of Sr with OLI predicted values

StdOrder	ICP - MS	OLI	Ratio	StdOrder	ICP - MS	OLI	Ratio
	mM	mM			mM	mM	
1	0.399	0.024	16.680	**28**	0.722	0.178	4.065
2	0.481	0.029	16.656	**29**	0.305	0.084	3.625
3	0.496	0.285	1.742	**30**	0.728	0.091	8.043
4	0.989	0.279	3.546	**31**	0.567	0.230	2.467
5	0.448	0.203	2.212	**32**	0.757	0.177	4.271
6	0.514	0.153	3.355	**33**	0.489	0.103	4.756
7	0.722	0.292	2.474	**34**	0.570	0.261	2.183
8	0.329	0.284	1.159	**35**	0.342	0.098	3.479
9	0.499	0.138	3.620	**36**	0.426	0.262	1.626
10	0.706	0.508	1.390	**37**	0.482	0.106	4.523
11	0.474	0.073	6.526	**38**	0.594	0.270	2.199
12	0.486	0.138	3.522	**39**	0.348	0.102	3.404
13	0.483	0.131	3.677	**40**	0.496	0.271	1.829
14	0.774	0.444	1.746	**41**	0.680	0.284	2.394
15	0.183	0.070	2.606	**42**	0.740	0.281	2.630
16	0.432	0.132	3.280	**43**	0.406	0.106	3.832
17	0.730	0.257	2.837	**44**	0.753	0.083	9.040
18	0.774	0.015	52.847	**45**	0.708	0.292	2.428
19	0.748	0.265	2.826	**46**	0.745	0.281	2.649
20	0.421	0.197	2.137	**47**	0.677	0.109	6.237
21	0.366	0.267	1.370	**48**	0.725	0.084	8.673
22	0.094	0.023	4.045	**49**	0.511	0.134	3.806
23	0.581	0.273	2.124	**50**	0.522	0.134	3.890
24	0.363	0.200	1.811	**51**	0.733	0.134	5.461
25	0.351	0.078	4.524	**52**	0.732	0.134	5.449
26	0.730	0.089	8.201	**53**	0.419	0.134	3.121
27	0.681	0.242	2.816	**54**	0.412	0.134	3.067

Ba

Table 40: Comparison of experimentally observed aqueous concentration of Ba with OLI predicted values

StdOrder	ICP - MS	OLI	Ratio	StdOrder	ICP - MS	OLI	Ratio
1	0.017	0.0002	71.434	**28**	0.050	0.0091	5.491
2	0.053	0.0020	26.935	**29**	0.002	0.0001	16.753
3	0.013	0.0003	50.609	**30**	0.053	0.0011	47.246
4	0.053	0.0020	26.970	**31**	0.002	0.0002	9.205
5	0.040	0.0003	131.822	**32**	0.052	0.0011	45.412
6	0.056	0.0020	27.892	**33**	0.052	0.0011	48.077
7	0.014	0.0003	41.157	**34**	0.020	0.0003	73.368
8	0.018	0.0020	8.656	**35**	0.003	0.0002	16.772
9	0.052	0.0012	42.935	**36**	0.006	0.0002	39.199
10	0.048	0.0013	36.850	**37**	0.051	0.0013	40.039
11	0.045	0.0011	39.805	**38**	0.023	0.0003	75.192
12	0.014	0.0013	10.786	**39**	0.003	0.0002	20.134
13	0.049	0.0002	300.060	**40**	0.013	0.0002	71.464
14	0.019	0.0002	103.736	**41**	0.022	0.0003	82.487
15	0.002	0.0002	13.888	**42**	0.053	0.0020	26.596
16	0.005	0.0002	27.893	**43**	0.004	0.0003	14.835
17	0.048	0.0002	206.939	**44**	0.053	0.0020	26.243
18	0.054	0.0002	236.103	**45**	0.019	0.0003	62.962
19	0.050	0.0003	162.378	**46**	0.053	0.0020	26.802
20	0.018	0.0003	61.625	**47**	0.030	0.0003	100.066
21	0.004	0.0003	14.586	**48**	0.053	0.0020	26.428
22	0.005	0.0003	18.233	**49**	0.011	0.0003	38.489
23	0.005	0.0003	14.328	**50**	0.007	0.0003	24.282
24	0.018	0.0003	53.436	**51**	0.050	0.0003	180.293
25	0.020	0.0011	18.440	**52**	0.049	0.0003	177.761
26	0.052	0.0089	5.808	**53**	0.019	0.0003	68.499
27	0.044	0.0014	30.624	**54**	0.016	0.0003	57.500

9.6. Analysis of stock solution

Table 41: Comparison of ICP-MS measured concentration for experimental stock solutions versus actual values

Sample Batch	**Concentration (mM)**			**Variation(%)**
	Target	Actual	Measured	
Batch 1				
$SrCl_2.6H_2O$	10	9.958	10.672	7.16%
$CaCl_2.2H_2O$	10	10.028	0.000	-100.00%
Na_2SO_4	10	10.088	37.032	267.11%
$MgCl_2$	10	10.108	11.412	12.90%
BaCl2.2H2O	10	9.992	10.243	2.52%
Batch 2				
$SrCl_2.6H_2O$	10	10.047	10.738	6.88%
$CaCl_2.2H_2O$	10	10.241	10.018	-2.17%
Na_2SO_4	10	10.119	0.000	-100.00%
$MgCl_2$	10	9.956	10.334	3.80%
$BaCl_2.2H_2O$	10	9.992	?	#VALUE!
Batch 3				
$SrCl_2.6H_2O$	10	9.808	10.491	6.96%
$CaCl_2.2H_2O$	10	10.173	18.648	83.31%
Na_2SO_4	10	9.965	0.000	-100.00%
$MgCl_2$	10	10.237	10.682	4.35%
$BaCl_2.2H_2O$	10	9.992	?	#VALUE!
Batch 4				
$SrCl_2.6H_2O$	10	100.256	105.304	5.04%
$CaCl_2.2H_2O$	10	99.721	0.000	-100.00%
Na_2SO_4	10	100.356	0.000	-100.00%
$MgCl_2$	10	100.254	132.013	31.68%
$BaCl_2.2H_2O$	10	9.992	9.924	-0.68%
Batch 5				
$SrCl_2.6H_2O$	10	100.256	100.710	0.45%
$CaCl_2.2H_2O$	10	99.721	102.241	2.53%
Na_2SO_4	10	100.356	0.000	-100.00%
$MgCl_2$	10	100.254	110.391	10.11%
$BaCl_2.2H_2O$	10	9.992	?	#VALUE!
Batch 6				
$SrCl_2.6H_2O$	10	100.256	99.103	-1.15%
$CaCl_2.2H_2O$	10	99.721	83.777	-15.99%
Na_2SO_4	10	100.356	0.000	-100.00%
$MgCl_2$	10	100.254	117.186	16.89%
$BaCl_2.2H_2O$	10	9.992	?	#VALUE!

9.7. Analysis of Initial Samples

Table 42: Comparison of ICP-MS measured concentration for initial samples versus actual values

	Actual Values (mM)						Measured Values (mM)				
StdOrder	**Sr**	**C**	**Ca**	**S**	**Mg**	**Ba**	**Mg**	**S**	**Ca**	**Sr**	**Ba**
1	0.5	0.75	0.25	1	1	0.05	0.541	7.018	0.000	0.242	0.028
41	0.75	0.5	1	1	0.25	0.05	0.423	4.581	4.696	0.743	0.053
25	0.75	0.75	0.25	0.25	1	0.05	1.164	3.791	3.464	0.742	0.052
9	0.5	0.5	1	0.25	1	0.05	0.964	3.188	0.000	0.488	0.051
33	0.5	0.75	1	0.25	0.25	0.05	0.240	4.570	0.000	0.486	0.052
35	0.5	0.75	1	1.75	0.25	0.05	0.160	3.248	0.000	0.261	0.027
49	0.75	0.75	1	1	1	0.05	0.688	5.066	2.419	0.419	0.031
51	0.75	0.75	1	1	1	0.05	0.971	3.691	0.000	0.739	0.050
53	0.75	0.75	1	1	1	0.05	0.666	0.000	0.093	0.475	0.034
18	0.75	1	0.25	1	0.25	0.05	0.274	0.000	2.256	0.728	0.052
20	0.75	1	1.75	1	0.25	0.05	0.270	0.000	1.874	0.633	0.045
10	1	0.5	1	0.25	1	0.05	1.098	0.000	1.300	0.941	0.048
2	0.5	0.75	0.25	1	1	0.05	0.062	6.950	1.769	0.480	0.052
42	0.75	0.5	1	1	0.25	0.05	0.019	9.901	2.628	0.737	0.053
26	0.75	0.75	0.25	0.25	1	0.05	0.025	7.657	2.101	0.723	0.051

9.8. Revised Experimental Considerations

1. Overall procedure is similar to what is described in Appendix 9.4.
2. Make use of nitrate salts instead of chloride salts
3. Measure equilibrium time directly and accurately to ensure precipitation has been finished
4. Perform experiments in an air-free set up. Use N_2 to sparge any air present in the set up
5. Add reagents through stock solutions of high concentration or directly as powder
6. Instead of relying on single measurement/detection technique, use multiple. For example, weighing the amount of final precipitate formed, pH and conductivity of the solution once equilibrium has been reached etc.

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