Preparation of synthetic water for flotation water analysis

McGill University
Department of Mining and Materials Engineering
Materials Engineering Co-op Program

MIME 280 Co-op Work Term Report

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1. EMPLOYER'S IDENTIFICATION

1.1. Employer Information

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2. WORKING ENVIRONMENT

2.1. Company Overview

As part of my MIME 280 Industrial Training course, I had the opportunity to work as a research intern at the Helmholtz Institute Freiberg (HIF) for Resource Technology in Freiberg, Germany. The HIF is a division of the Helmholtz-Zentrum Dresden-Rossendorf (HZDR), a research laboratory and member of the Helmholtz Association of German Research Centres which is the largest scientific organization in Germany. The HIF conducts research in the fields of energy efficiency, materials, and resource technology within the divisions of Analytics, Exploration, Extraction, Metallurgy and Recycling, Modelling and Evaluation, and Processing. The main objective of the HIF is to improve on and develop innovative technologies for the economical and efficient extraction and separation of mineral and metalliferous raw materials, while working in close collaboration with the Technische Universität Bergakademie Freiberg (Freiberg University of Mining and Technology) and German industry partners (Helmholtz-Zentrum Dresden-Rossendorf, 2017).

2.2. Job Description

The Division of Processing at the HIF conducts research predominantly in the field of froth flotation, in the areas of: atomic force microscopy, hydrodynamics, interfacial phenomena, modelling, ultra-fine particle flotation, and water quality. As a research intern in the Division of Processing, headed by Dr. Martin Rudolph, I was part of a main project concentrated on the impact of water quality on flotation performance, which is an integral part of Mr. Bruno Michaux's PhD thesis. Given this I worked directly with Mr. Michaux, meeting weekly if not daily to go over results and future plans. Following an initial literature review on Mr. Michaux's research topic, I was given a long-term project to determine a method of preparing reproducible synthetic water for the use in subsequent flotation water analysis. I was entrusted with this task and given the freedom and resources to finalize my method by the expected start date of flotation experiments. This

process included an extensive literature review on water chemistry topics and water testing methods which continued throughout the length of the project. My daily tasks varied from day to day, but a great deal of time was spent running laboratory experiments and analyzing data. Relying on scientific sources and the knowledge of and collaboration with Mr. Michaux, different water preparation methods were tried and tested, subsequently analyzed and modified, before a final method was finalized and scaled up to meet the demands of froth flotation experiments. The contents of this report were presented in presentation format to my supervisors and fellow colleagues on August 8, 2017.

3. WORK UNDERTAKEN

Abstract

A natural water source in Germany, used as the main water source of an industrial scale flotation circuit, is analyzed for its ion concentration and is set as the target for synthetic water reproduction. Thus, presented in this study is the preparation of synthetic water to be used in future flotation water analysis. The importance of natural water chemistry is evaluated and an emphasis is placed on the role of CO_2 and the carbonate system. As a conservative quantity, alkalinity is an efficient method to quantify changes in water composition. Alkalinity is thus determined by two widely used titration analysis methods (titration to pH ~4.5 using the fixed endpoint method and the inflection point method). It is determined that titration using the fixed endpoint method can lead to an overestimation of the bicarbonate ion concentration given the higher equivalence point of the natural water source analyzed. Using a combination of modelling software and batch experiments, the preparation of synthetic water is finalized before scaling up to prepare 25 L of synthetic water for flotation experiments. A suggested experimental setup is also described. Reproducible and consistent results are achieved and results obtained agree well with the expected bicarbonate concentration of the final synthetic water recipe. However, the target $[HCO_3^-]$ is not achieved due to the presence of other titratable ions in natural water.

3.1. Introduction

Water constitutes 80-85% of the total volume of mineral pulp processed in froth flotation circuits (Levay & Skinner, 2001) with most water coming from natural water sources. Flotation is most effectively undertaken with fresh water (Liu et al., 2013), however, there is a growing need for water reuse in the mineral processing industry due to fresh water scarcity and environmental regulations on discharged water (Wang & Peng, 2014). Naturally, water recirculation results in a decline in water quality and consequently in process performance. Therefore, studies on the impact of water quality on flotation efficiency seek to understand issues associated with water reuse as a direct result of the subsequent water composition changes during the flotation process. Water chemistry models capable of predicting these effects can be powerful decision-making tools for plant operators, helping them identify and quantify the impact of process water recirculation. As a result, this would enable the implementation of water-saving strategies as outlined in Figure 1 (Michaux et al., 2017).
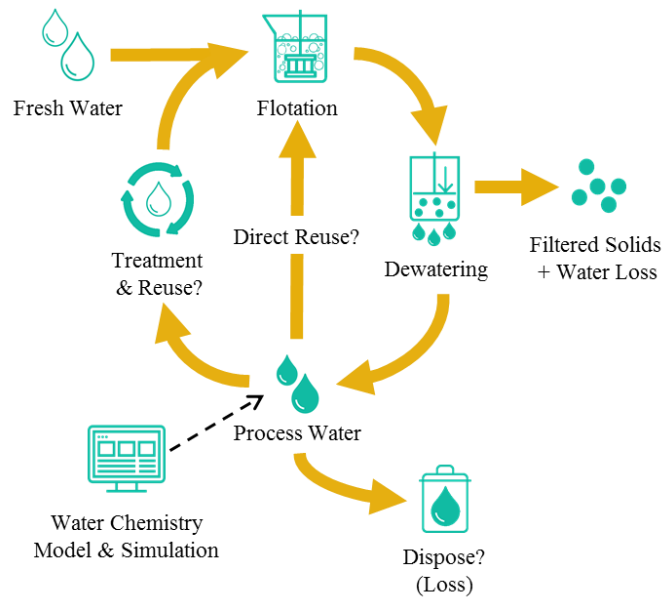

Figure 1 – An Example of a Water-Saving Strategy for an Industrial Scale Flotation Plant with the Role of a Water Chemistry Model Illustrated (Michaux et al., 2017)

For the study described above, and the modelling of changes in water chemistry, it is essential to have a consistent and reproducible water source with known composition of major and minor constituents. This is most easily achieved by producing synthetic water with a replicated composition similar to that of the natural water source to be studied. This is done by preparing stock solutions of highly soluble salts, which can be combined to prepare synthetic water of desired composition. This practice has been used extensively in the marine sciences for seawater analysis (Berges et al., 2001).

However, unlike synthetic seawater, which has been studied extensively and a standard recipe that has been developed over time with only minor changes, there is no standard protocol for the preparation of synthetic natural water. This is because the composition of natural water can vary significantly depending on the water source (Sugiyama et al., 2016). Organic makeup, geology and other factors give rise to natural waters with varying values of pH, alkalinity, ion concentrations, organic and mineral content, hardness, and salinity. This can be seen in Table 1, which lists the water composition of different natural water sources (Livingstone, 1963). Furthermore, the chemistry of the same water source can differ greatly due to interaction with rain water, evaporation at the surface, sedimentation, and other processes. Natural water can also have significant seasonal variation due to biological activities such as photosynthesis and respiration.

Table 1 – Water Composition of Different Natural Water Rivers Given in mol/L (Livingstone, 1963)

River	Na^+	Ca^{2+}	Mg^{2+}	K^+	Cl^-	SO_4^{2-}	HCO_3^-
Rio Grande	1.98×10^{-3}	1.47×10^{-3}	4.73×10^{-4}	1.20×10^{-4}	1.23×10^{-3}	1.08×10^{-3}	2.553×10^{-3}
Ohio	7.50×10^{-4}	8.68×10^{-4}	3.3×10^{-4}	7.3×10^{-5}	6.06×10^{-4}	9.11×10^{-4}	8.44×10^{-4}
Seine	3.2×10^{-4}	1.8×10^{-3}	6.6×10^{-5}	5.6×10^{-5}	2.1×10^{-4}	2.27×10^{-4}	3.31×10^{-3}
Mekong	3.7×10^{-4}	7.76×10^{-4}	2.3×10^{-4}	4.3×10^{-5}	1.8×10^{-4}	1.53×10^{-4}	1.895×10^{-3}

Synthetic water gives the added benefit of minimizing biological effects, which are difficult to analyze and can have a significant effect on the equilibrium of the system (Herczeg et al., 1985). Other reasons for the use of synthetic water can be due to difficulty in accessing the natural water source or a lack of supply. Finally, synthetic

water allows the researcher to manipulate major and minor constituents much more easily, while being beneficial to others who need to run similar experiments.

For this study, a natural water source in Germany is analyzed for its chemical make-up using inductively coupled plasma mass spectrometry (ICP-MS) for cation determination and ion chromatography (IC) and spectrophotometry for anion determination. The $[HCO_3^-]$ is determined through alkalinity titration. Table 2 lists the composition of this water source with major constituents: Ca^{2+}, Mg^{2+}, Cl^-, Na^+, $HCO3^-$ and minor constituents: K^+, NO_3^-, SO_4^{2-}, F^-, PO_4^{3-}. Other constituents were neither detected nor analyzed. This water is set as the target composition for all future synthetic water preparation.

Table 2 – Water Composition of a Natural Water Source in Germany

Ion	Ca^{2+}	Mg^{2+}	F^-	SO_4^{2-}	Cl^-	NO_3^-	Na^+	K^+	PO_4^{3-}	HCO_3^-
Concentration (mg/L)	8.30	2.86	0.11	<1	7.20	1.17	6.50	1.70	0.05	51.87
Concentration (mmol/L)	0.207	0.118	0.006	<0.01	0.203	0.019	0.283	0.043	0.001	0.85

The goal of this project is to outline the preparation method of synthetic natural water which can be used as a medium for froth flotation experiments and a method of analyzing the water to ensure it is consistent and reproducible. A thorough literature review is provided to give the reader a basic overview of important water chemistry concepts. This report can be beneficial to anyone looking to prepare synthetic water for flotation experiments or any other mineral processing operations where water is used as a transport or process medium.

The final preparation method for 25 L of synthetic water used for flotation experiments is outlined in the experimental methods section of this report. This water is used for all aspects of the flotation circuit, which includes: milling of the feed, flotation medium, wash/top-up water etc. This report also places an emphasis on the methodology and different iterations of 1 L batch synthetic water which was used to finalize the preparation method.

3.1.1. Problem Statement

Although literature is limited, references are available for synthetic natural water preparation with the two main sources resulting from the work of Smith et al. (2002) and Sugiyama et al. (2016). However, the main objective of this selected work was to replicate natural water sources without any subsequent use of the synthetic water as a medium for future analysis. Therefore, little attention is given to important water chemistry topics such as the carbonate system and titration alkalinity. Furthermore, without a background in water chemistry, it is difficult to comprehend some key experimental decisions made related to the inorganic chemistry of dissolution, such as solubility, precipitation, and the use of CO_2 bubbling. Finally, little has been written on preparing synthetic water to the scale of laboratory flotation experiments. Problems encountered during the water preparation process and scale up procedure are outlined and suggestions are made to avoid these issues. It is my hope the reader can benefit from these findings and listed references, and have a starting point to develop their own method for the preparation of synthetic natural water.

3.2. Literature Review

3.2.1. Natural Water Chemistry

Knowledge of water chemistry is important in understanding processes concerning natural water and quantifying changes in composition. For natural waters, two inorganic carbon transfer processes are important: (1) CO_2 exchange across the air-water interface, and (2) The precipitation/dissolution of $CaCO_3$ (Howard et al., 1984). The main source of bicarbonate in natural water concerns both of these processes and is due to atmospheric CO_2 and the weathering of carbonate minerals such as calcite in rocks and soil. For the purposes of this report, two key chemical reactions are predominant and must be understood: acid/base reactions and dissolution/precipitation reactions (Pankow, 1991). Equation 1 is an example of an acid/base reaction, the dissociation of bicarbonate.

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad\qquad (1)$$

The dissolution of calcite is outlined in Equation 2.

$$CaCO_{3(s)} \rightleftharpoons CO_3^{2-} + Ca^{2+} \qquad\qquad (2)$$

The other important topic concerning natural water is biological effects such as photosynthesis and respiration which can have a significant effect on the equilibrium of the system. As decribed by Herczeg et al. (1985), lakes may have their pH driven significantly higher during phytoplankton blooms because of the photosynthetic consumption of CO_2. This directly results in a lower P_{co2} and can therefore lead to a decrease in dissolved calcium and alkalinity due to the precipitation of carbonate minerals. The pH dependence on P_{co2} can be easily seen in Figure 2 and this relationship is further described by the system of equations of the carbonate system presented in the following subsection.
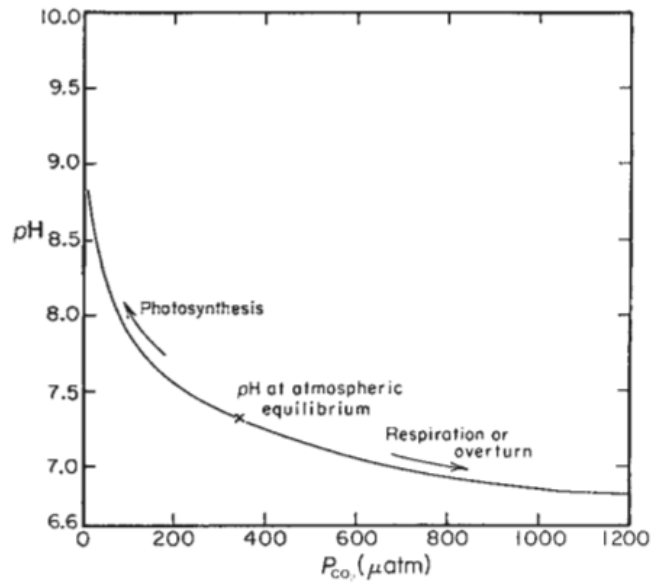

Figure 2 – pH Dependence on P_{co2} for a Northwestern Ontario Lake (Herczeg et al., 1985)

Given these perturbations and the difficulty in assessing organic materials, biological effects are avoided and are not of a concern for the preparation of synthetic water. However, biological effects must be considered when quantifying differences between the composition of a natural water source and its synthetic water reproduction.

3.2.2. Dissolved CO₂ and the Carbonate System

The chemistry of natural waters is heavily influenced by atmospheric CO_2 and the carbonate system. As summarized by Pankow (1991), atmospheric CO_2 can dissolve in water according to the reaction

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \tag{3}$$

where $CO_{2(aq)}$ represents dissolved CO_2, which can itself react with water to form carbonic acid (H_2CO_3)

$$H_2CO_3 \rightleftharpoons CO_{2(aq)} + H_2O \tag{4}$$

with any dissolved CO_2 having the potential to react with water to produce more H_2CO_3. Therefore, in most water chemistry text, the concentration of $H_2CO_3{}^*$ is usually defined according to Equation 5.

$$[H_2CO_3^*] = [CO_{2(aq)}] + [H_2CO_3] \tag{5}$$

The diprotic acid, H_2CO_3, can dissociate twice according to Equations 6 & 7 (neglecting activity corrections).

$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^- \qquad K_1 = \frac{[HCO_3^-][H^+]}{[H_2CO_3^*]} \tag{6}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \tag{7}$$
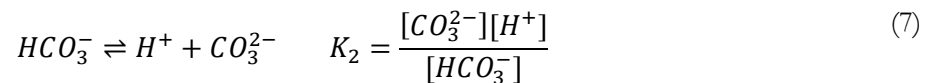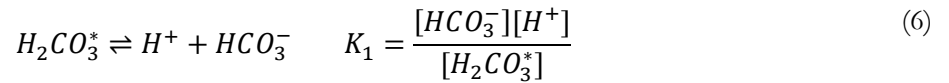
The carbonate system can therefore be concluded as the equilibrium between

$$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+ \qquad (8)$$
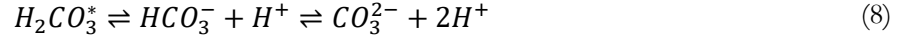
and the entire system can be represented visually by Figure 3.
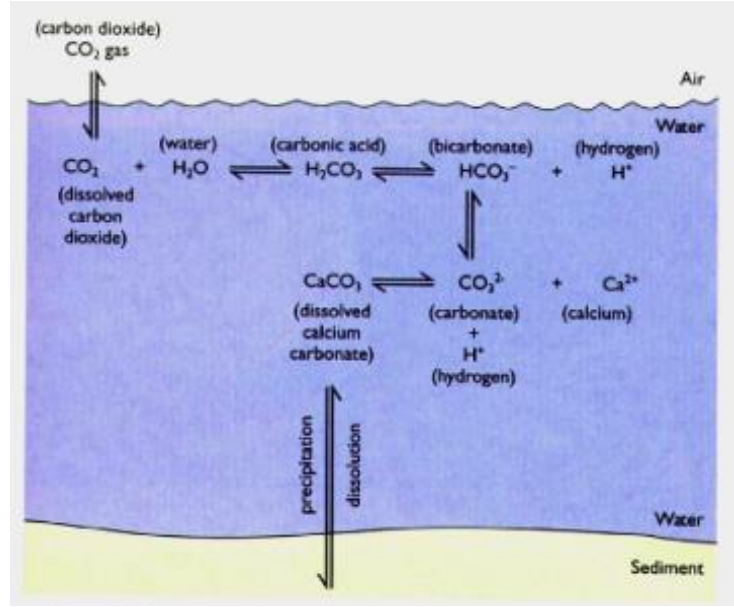
Figure 3 – The Carbonate System (Morse & Mackenzie, 1990)

This system has an important function in acting as a buffer to regulate water systems and plays a fundamental role in many geological, chemical, and biological processes. A good understanding of the carbonate system allows researchers to study the effects of these different water chemistry processes and/or manipulate the system to fit their needs.

For an open aqueous system in equilibrium with the atmospheric CO_2, the CO_2 solubility follows Henry's Law (neglecting activity corrections)

$$[H_2CO_3^*] = K_H P_{CO_2} \qquad (9)$$

where K_H is the Henry's Law constant for CO_2.

Given this relationship, the system can be easily perturbed by changing the P_{co_2}, which brings forth a new equilibrium with respect to the whole carbonate system. This will of course result in different pH values and carbonate speciations. This can be seen by the carbonate species diagram in Figure 4. It is important to note, however, that at constant P_{co_2}, $[H_2CO_3]$, $[CO_2]$, and $[HCO_3^*]$ are independent of pH and are therefore constant.

For the purposes of this study, the P_{co_2} is manipulated through the bubbling of CO_2 in solution for two important reasons: (1) To speed up the conversion of OH^- to HCO_3^- from the addition of $Ca(OH)_2$, and (2) To promote the dissolution of $CaCO_3$.

The addition of hydroxide causes bicarbonate to convert into carbonate and carbonic acid to convert into bicarbonate according to Equations 10 & 11.

$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O \qquad (10)$$

$$H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O \qquad (11)$$

The solution is now deficient in H_2CO_3, therefore, the water proceeds to absorb CO_2 from the atmosphere through the backward reaction shown in Equation 4. The net result is an increase in HCO_3^- and CO_3^{2-}. For objective (1), this process can be sped up by increasing the P_{co_2} by means of bubbling CO_2 into the solution.

For the preparation of synthetic water, $CaCO_3$ precipitation is avoided, however, as atmospheric CO_2 reacts with $Ca(OH)_2$ this can also lead to the formation of an unwanted calcium carbonate impurity. Increasing the P_{co_2} brings the solution to acidic conditions through the disassociation of carbonic acid and can therefore lead to the desired effect of increasing the solubility of $CaCO_3$ given that solubility is highly pH dependent for insoluble salts. This is also achieved by bubbling CO_2 into the solution, and as deduced from the system of equations above, the increase in P_{co_2} directly results in a lowering of pH. This satisfies objective (2), promoting the dissolution reaction as shown by Equation 2 and discouraging the precipitation of $CaCO_3$.

The carbonate system can be further defined by measuring the total concentration of carbon dioxide-related species (C_T), and the related dissociation constants. However, due to the difficulty of accurately measuring these

parameters, and the ability to quantify changes in water by measuring alkalinity, these values are not measured. Temperature-influence also has an effect on the solubility of CO_2, however, this effect is minor and is not considered because of insignificant changes in temperature in the laboratory.
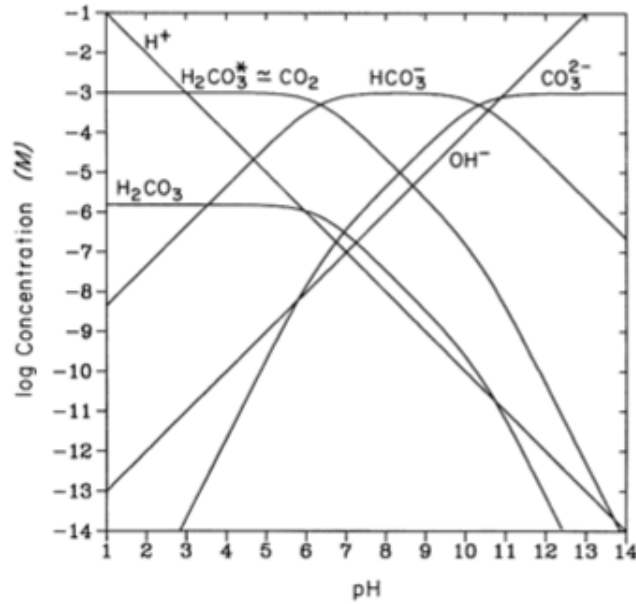
Figure 4 – Carbon Dioxide Speciation as a Function of pH at 25 °C/1 atm for $C_T = 10^{-3}$ M (Pankow, 1991)

3.2.3. Alkalinity

Alkalinity is the preferred measurement to quantify changes in water. As defined by White (2013), alkalinity is a measure of acid-neutralizing capacity of a solution and is defined as the sum of acid necessary to titrate all the weak bases in solution to the bicarbonate equivalence point, also called the second equivalence point. It can also simply be considered as the difference between conservative cations and anions. The total alkalinity (Dickson, 1981) can be written mathematically as

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] \quad (12)$$

$$+ [HS^-] + 2[S^{2-}] + [NH_3] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4]$$

with borates, phosphates, silicates, and other organic bases present in water. However, for most natural waters, the concentrations of these bases are sufficiently low and can be considered negligible in comparison to the bicarbonate concentration. As the weak-acid anions are dominated by the carbonate system, total alkalinity can be simplified in terms of the carbonate alkalinity, A_c.

$$A_C = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (13)$$

At the pH range of most natural waters, bicarbonate is the dominant carbonate species present as shown in Figure 4. Therefore, the total alkalinity can be assumed to be equal to the concentration of bicarbonate. The individual terms of Equation 13, themselves are not conservative, but are dependent on pH and their respective dissociation constants. However, the total alkalinity is a conservative quantity of the system and is independent on temperature and pressure (Munhoven, 2013). Alkalinity is usually given in units of millimoles per litre, milliequivalents per litre, or ppm CaCO$_3$.

For the purposes of the preparation of synthetic water and the bubbling of CO$_2$ in solution, it is important to note that total alkalinity is conserved with the addition of CO$_2$. For every H$^+$ ion that is added from the dissociation of H$_2$CO$_3$ that reduces alkalinity, a HCO$_3^-$ ion adds 1 unit of alkalinity, thus cancelling each other out. This is not the case with the addition of a strong acid, such as HCl, as this decreases the total alkalinity. The other undesired effect, leading to a variation in alkalinity, is the direct result of the dissolution/precipitation of calcium carbonate. Therefore, it is important to assure total dissolution of any calcium carbonate present, and to avoid any precipitation of calcium carbonate which decreases the total alkalinity.

3.2.4. Titration

Alkalinity is determined by titration of a water sample with a standard solution of a strong acid (e.g., HCl) to the bicarbonate equivalence point, where

$$[HCO_3^-] \cong [H^+] \tag{14}$$

with the endpoint detected either by potentiometric titration using a pH meter or by coulometric titration using colour-changing indicators. Titration is usually carried to a single end point (most commonly to pH ~4.5) using the fixed endpoint method as for most natural waters this gives sufficiently accurate results. However, given that the true equivalence point pH for dissociation of the bicarbonate ion to carbonic acid varies with the total alkalinity (Thomas & Lynch, 1960), and as shown by Figure 5, a far more accurate result can be achieved by using the inflection point titration (IPT) method. A titration curve is produced by plotting pH versus volume of titrant added and the endpoint is determined from the inflection point of the resulting curve by finding the greatest change in pH per ml of acid added. Titration is thus carried out to either desired endpoint and calculated by the following equation (International Standards Organization, 1994)

$$A_T = \frac{c(HCl)V_{HCl}1000}{V_{SW}} \tag{15}$$

where $c(HCl)$ is the actual concentration of hydrochloric acid solution expressed in moles per litre, V_{HCl} is the volume in milliliters of the hydrochloric acid solution consumed to reach the equivalence point, and V_{SW} is the volume in milliliters of the synthetic water test portion. A_T is given here in units of mmol/L.

Accurate results can be obtained from simple laboratory equipment (glass burette, pH electrode, magnetic stirrer) with titration usually carried out on filtered samples to avoid interference from suspended particles (Grasshoff et al., 1999). It is important to note that it is not necessary to start a titration immediately in order to avoid the effects of CO_2 exchange, as CO_2 converts to bicarbonate just as fast as it leaves the solution. However, samples should be stored and capped to avoid contamination and excessive evaporation.
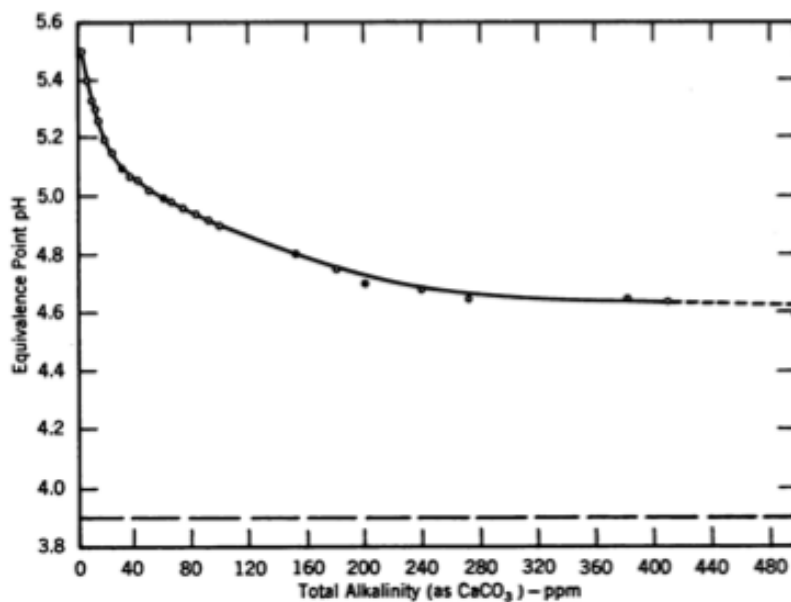
Figure 5 – Variation of Equivalence Point pH with Total Alkalinity (Thomas & Lynch, 1960)

3.3. Experimental Methods

3.3.1. Materials

All salts considered for synthetic water preparation are listed in Table 3. With the exception of the calcium hydroxide used for batch synthetic water preparation, all salts were of reagent grade (Carl Roth, Germany). High grade reagents were chosen to minimize the influence of impurities. For all synthetic water prepared after SWF-2, NaF and $NaNO_3$ were oven dried at 110 °C for 2 hours due to their hygroscopic nature. They were then placed in a desiccator to cool before being weighed. As suggested by Kester et al. (1967), the hydrated forms of $MgCl_2$, $CaCl_2$, and $MgSO_4$ were chosen due to the difficulty of weighing the anhydrous form of these salts which may contain differing degrees of hydration. $NaHCO_3$ and $KHCO_3$ were not oven dried due to their low decomposition temperatures.

Table 3 – Laboratory and Commercially Available Salts

Salt	Molar Mass (g/mol)	Solubility* (g/L, H_2O, 20 °C)
$CaCl_2 \cdot 2H_2O$	147.02	1000
$Ca(OH)_2$†	74.09	1.7
$CaCO_3$	100.09	0.014
CaO	56.08	dec.
$KHCO_3$	100.12	333
$MgCl_2 \cdot 6H_2O$	203.30	1670
MgO	40.30	ss
$MgSO_4 \cdot 7H_2O$	246.48	710
Na_2CO_3	105.99	220
Na_2SO_4	142.04	170
$NaCl$	58.44	358
NaF	41.99	42
$NaHCO_3$	84.01	95.5
$NaNO_3$	84.99	874

Laboratory deionized (DI) water was used for all water preparation. A pH glass electrode and pH meter (model pH 110, VWR, U.S.A.) was used for all pH measurements and calibrated using buffers with pH values 4, 7, and 10. The water preparation apparatuses consisted of a 1 L glass reactor (Trallero and Schlee, Spain), 30 L PE Drum (Mauser, Germany), 30 L HDPE storage tank (Speidel, Germany), mechanical stirrer (Phoenix Instrument, Germany), air pump with diffuser (EHEIM, Germany), and CO_2 tank kit (JBL, Germany). The following equipment was used for alkalinity titration: 25 ml burette (Duran, Germany) graduated in divisions of 0.05 ml, 10 ml precision burette (Duran, Germany) graduated in divisions of 0.02 ml, magnetic stirrer (IKA, Germany) and magnetic stir bar (Carl Roth, Germany).

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* ss denotes sparingly soluble, dec. denotes decomposes. Solubility data was retrieved from the supplier.

†† $Ca(OH)_2$ used in the preparation of SWB-1-7 was prepared in the laboratory from the precipitation reaction between $CaCl_2$ and NaOH. The $Ca(OH)_2$ precipitate was filtered and oven dried before being placed in a desiccator. All future synthetic water was prepared using reagent grade $Ca(OH)_2$ (Merck, Germany).

3.3.2. Synthetic Water Recipe

Given the major water composition of the natural water source listed in Table 2, and the list of available salts listed in Table 3, a matrix was created in Microsoft Excel (2016) to design a water recipe which could come closest to matching the ion composition of the natural water source. Salts were selected on the basis of solubility, purity, and their laboratory or commercial availability. The first salts selected where those which satisfied the addition of the minor constituents: F^-, K^+, NO_3^-, and SO_4^{2-} as these species were satisfied by the addition of only one salt. Phosphate ion addition was not considered due to its insignificant concentration and consequently its negligible influence on the water chemistry. NaF, $NaNO_3$, and $KHCO_3$ were selected as the sole sources of F^-, NO_3^- and K^+, respectively. Sulfate ions were not detected due to being under the detection limit of the apparatus, however, as sulfate ions are present in most natural waters as a major constituent, a concentration of 5×10^{-3} mmol/L (half the detection limit of the apparatus) was added and satisfied by the addition of $MgSO_4 \cdot 7H_2O$.

The next step was to satisfy the addition of the major constituents: Ca^{2+}, Cl^-, Mg^{2+}, Na^+, and HCO_3^-. The original synthetic water iteration included MgO as the main source of Mg^{2+} and $CaCl_2 \cdot 6H_2O$ as the main source of Cl^-. This allowed the synthetic water recipe to exactly match the weight composition of the targeted natural water. However, the recipe was adjusted to avoid the use of MgO, which is only sparingly soluble. Therefore, $MgCl_2 \cdot 2H_2O$ was selected to meet the remaining amount of Mg^{2+} required. For this reason, the final synthetic water recipe, hereinafter referred to as SW, has a higher concentration of Cl^- in comparison to the target value. This was deemed a satisfactory result, due to the difficulty and uncertain results in dissolving MgO. The remainder of Na^+ was met by the addition of $NaHCO_3^-$.

As encountered by Smith et al. (2002) and Sugiyama et al. (2016), the main difficulty in preparing synthetic natural water is the addition of calcium and bicarbonate through the dissolution of one of the carbonate containing calcium salts: $CaCO_3$, CaO, $Ca(OH)_2$. As calcium carbonate is both a main source of Ca^{2+} and HCO_3^- in natural water, the logical choice was to dissolve $CaCO_3$, however, due its low solubility, $CaCO_3$ was abandoned in favour of using $Ca(OH)_2$. $Ca(OH)_2$ was selected over CaO, due its higher-grade availability. The

ion composition with expected HCO_3^- concentration of the final SW water recipe concentration and a comparison with the natural water source can be found in Table 4.

Table 4 – Ion Comparison of SW Recipe and Natural Water

Ion	Ca^{2+}	Mg^{2+}	F^-	SO_4^{2-}	Cl^-	NO_3^-	Na^+	K^+	PO_4^{3-}	$HCO_3^{-\ddagger}$
SW Concentration (mmol/L)	0.207	0.118	0.006	0.005	0.226	0.019	0.283	0.043	0	0.715
Difference (mmol/L)	0	0	0	-	**0.023**	0	0	0	-	**-0.135**

As water is electrically neutral, the sum of cations must equal the sum of anions to maintain charge balance. Due to this, it was not possible to match the bicarbonate concentration without significantly increasing the concentration of one or more of the major cations: Na^+, K^+, Ca^{2+}. Therefore, the SW recipe has a lower weighed $[HCO_3^-]$ than the natural water source. This decision is elaborated and justified in the discussion section of this report.

The proton balance equation (PBE) for this water recipe can be defined according to Equation 16.

$$[Na^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + [K^+] \quad (16)$$
$$= [Cl^-] + 2[SO_4^{2-}] + [NO_3^-] + [F^-] + [HCO_3^-] + [OH^-]$$

3.3.3. Preparation of Stock Solutions

The following procedure is derived from the work of Smith et al. (2002). As suggested, salts were grouped together in compatible combinations to avoid the precipitation of insoluble compounds. This was confirmed

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‡ $[HCO3^-]$ is calculated as $[NaHCO_3] + [KHCO_3] + 2[Ca(OH)_2]$, which is also the charge balance between cations and anions for the synthetic water recipe.

by using the chemical equilibria software Visual MINTEQ (Gustafsson, 2016). The program requires an input of each of the major ions and calculates species distributions and saturations indexes using thermodynamic equilibrium techniques. Given that we are working with an open system; CO_2 was included as one of the species with an input value of 3.8×10^{-3} atm. The model output concluded a minimum of 3 stock solutions required so as to avoid the precipitation of $CaCO_3$, $CaSO_4$, and other insoluble minerals. Table 5 lists the final stock solutions used for the preparation of 25 L of SW. SS-1 includes the following salts: $NaHCO_3$, $KHCO_3$, NaF, and $NaNO_3$. SS-2 consists of $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$. SS-3 consists exclusively of $Ca(OH)_2$. SWB-1-5 were prepared with SS-1 of concentration factor x100, SS-2A (consisting of the anhydrous form of $MgCl_2$) x100, and SS-4 (consisting of Na_2SO_4) x100 stock solutions, due to unavailability of some salts at the time.

Table 5 – Synthetic Water Stock Solutions

Stock Solution	Mass (g) per 1 L§ of DI Water	Conc. Factor	Volume (ml) Required to Prepare 25 L of SW
SS-1			
$NaHCO_3$	5.41864		
$KHCO_3$	1.07629	x250	100
NaF	0.06298		
$NaNO_3$	0.4037		
SS-2			
$MgCl_2 \cdot 6H_2O$	5.74322	x250	100
$MgSO_4 \cdot 7H_2O$	0.6162		
SS-3			
$Ca(OH)_2$	0.38342	x1	~ 2000

Stock solutions SS-1 and SS-2 were made up to a concentration factor of x250 for various reasons. Firstly, it is far more accurate and easier to weigh salts in g than mg, and in some cases the weight required would be greatly impacted by the accuracy of the scales. Also, higher concentrations of ions in the stock solution ensure that they are relatively free from contamination. Finally, it allows for many synthetic water solutions to be prepared

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§ SS-1 and SS-2 were prepared in 2 L volumetric flasks.

from the same stock solutions, allowing for consistency between prepared waters. However, too great of a concentration would require a large amount of solute, resulting in a waste of material and a longer dissolution time. More importantly, the concentrations should not exceed the solubility limit of the salts so as to avoid oversaturation. This was again confirmed in Visual MINTEQ before proceeding. A concentration factor of x250 was found to be optimal to allow for 100 ml of each stock solution to make up the final 25 L solution. This volume was measured using glass volumetric pipettes which are readily available in the laboratory. The preparation of SS-1 and SS-2 simply involved dissolving the correct weight of each salt with DI water in glass volumetric flasks. All salts dissolved readily and no mechanical mixing was required. The stock solutions were capped and stored out of direct sunlight. New stock solutions were prepared monthly.

SS-3 was not stable at high concentration due to its oversaturation with respect to calcium carbonate minerals. For this reason, SS-3 was made at x1 concentration the day of water preparation. To break up agglomerates, the solution was placed in an ultrasonic bath for a minimum of 10 minutes before it was diluted further. Due to its slight solubility, calcium hydroxide is present as a fine suspension. Therefore, the flask is thoroughly rinsed after addition.

3.3.4. Batch Synthetic Water Preparation

Before the synthetic water was prepared to 25 L flotation scale, 1 L synthetic water batch (SWB) experiments were performed in a 1 L glass reactor, as shown in Figure 6, to finalize the preparation method before proceeding. Most importantly a method to increase the kinetics of the carbonate conversion and equilibrium with the atmospheric CO_2 was required. Different options to equilibrate the water were considered: (1) The addition of a strong acid such as HCl, (2) Allowing the solution to equilibrate with the atmospheric CO_2 naturally, (3) Aerating the solution with laboratory compressed air, and (4) Bubbling of CO_2 followed by air bubbling to remove the excess dissolved CO_2 in the solution. Option 1 was no longer considered after the literature review confirmed the addition of a strong acid would decrease the total alkalinity. Option 2 was attempted for the preparation of SWB-2, however, the kinetics proved to be too long and unreliable. Option 3

was believed to be the best course of action due to the availability of laboratory compressed air; in addition, the literature review confirmed aerating would bring forth equilibrium in much less time than leaving the solution to equilibrate on its own. SWB-1 and SWB-4 were prepared beforehand before aeration, whereas, for SWB-3 and SWB-5, the $Ca(OH)_2$ solution was bubbled initially with air before the addition of the other stock solutions. However, with all four waters, the modelled equilibrium pH value was not reached. Finally, SWB-6 and SWB-7 were bubbled with CO_2 followed by aeration. However, it was determined that the P_{co2} of the compressed air was insufficient and an air pump was used for aeration of SWB-7. This was the final SWB iteration before scaling up to 25 L flotation scale. Graphs of pH vs time were plotted for each SWB preparation, and samples were taken and analyzed for alkalinity titration.

Figure 6 – 1 L Synthetic Water Batch (SWB) Apparatus

3.3.5. 25 L Flotation Synthetic Water Preparation

Synthetic water for flotation (SWF) was prepared weekly in a 30 L PE Drum and stored in a 30 L HDPE storage tank for future use. The setup, shown in Figure 7, includes the following: mechanical stirrer, air pump with diffuser, CO_2 tank and accessories (pressure regulator, solenoid, diffuser, and bubble counter). Before water preparation, the tank and diffusers are thoroughly rinsed with DI water. Approximately 22 L of DI water is added to the tank and the stirrer is turned on to promote dissolution. The tank is then bubbled with CO_2 gas to titrate the solution to acidic conditions. This step is important to avoid precipitation of insoluble compounds, to increase the solubility of any calcium carbonate impurity, and finally to promote the conversion of OH^- into HCO_3^-. This takes approximately 1 hour at a flow rate of around 5 bubbles per second. During this time, the $Ca(OH)_2$ solution is prepared to around 2 L in a volumetric flask. After the appropriate CO_2 bubbling time, the $Ca(OH)_2$ solution is added slowly to the tank using a funnel to avoid spillage. Given that $Ca(OH)_2$ is still in suspension, the volumetric flask is thoroughly rinsed into the tank to ensure any undissolved particles enter the solution. It is also important to rinse the sides of the tank and any air tubes present inside the reactor. The addition of the $Ca(OH)_2$ increases the pH to ~6. At this stage CO_2 bubbling is turned off and the other stock solutions are added. Using volumetric pipettes, 100 ml of each stock solution is added slowly with vigorous mixing. This increases the pH slightly. The sides of the tank are thoroughly rinsed again and the solution is diluted with DI water to the final 25 L using a laboratory scale. The solution is approximated to a density of 1.0 g/ml. Finally, the solution is bubbled with air to stabilize the solution and to remove any excess CO_2 bringing the P_{CO_2} to near atmospheric concentration. This takes approximately 2 hours. The preparation of 25 L of synthetic water can be completed within half a day. Synthetic water for flotation is prepared weekly and analyzed for alkalinity, with select samples analyzed for ion concentration.

Figure 7 – Synthetic Water for Flotation (SWF) Apparatus

3.3.6. Analyses

Water samples were filtered through 0.45 μm cellulose nitrate filter membranes (Sartorius, Germany) before titration. The titration method used is described in (International Standards Organization, 1994) including the standardization procedure of 0.02 M HCl. The titration set-up is shown in Figure 8. The pH meter was first calibrated to acidic conditions, as the accuracy of the pH measurement is highest in the area at which the pH electrode is calibrated. A few important assumptions are made: 1) CO_2 outgassing during titration is neglected and 2) the sample temperature was approximated to 20 °C. Temperature was not maintained, however, due to the length of the procedure, the temperature is assumed to be constant. SWB samples were titrated using the fixed endpoint method to pH ~4.5 using a 25 ml glass burette. SWF samples were titrated using both the fixed endpoint method and the IPT method using a 10 ml precision burette. All test samples were of 100 ml. Select synthetic water samples were analyzed for ion concentration using ICP-MS for cation determination and IC/spectrophotometry for anion determination.

Figure 8 – Alkalinity Titration Apparatus

3.4. Results and Observations

3.4.1. Modelling Output

Ion concentration values listed in Table 2 were input into Visual MINTEQ along with an input temperature of 20 °C and P_{co2} value of 3.8 x 10^{-3} atm. The model output determined an equilibrium pH of 8.04 for the SW recipe. This pH value was used as a target for all synthetic water preparation. Table 6 lists the carbon dioxide speciations for this defined water composition, which confirms bicarbonate as the dominant species accounting for almost 97% of the total carbonate concentration. Output tables for calculated saturation indexes and mass distribution of dissolved and precipitated species resulted in undersaturation with respect to all mineral components and 0% precipitation, respectively.

Table 6 – Visual MINTEQ Model Output

CO_3^{2-} Species	% of Total Concentration
CO_3^{2-}	0.503
HCO_3^-	96.985
$H_2CO_3^*$ (aq)	2.055
$MgCO_3$ (aq)	0.033
$MgHCO_3^+$	0.096
$CaHCO_3^+$	0.198
$CaCO_3$ (aq)	0.114
$NaHCO_3$ (aq)	0.014

3.4.2. Comparison of Batch Synthetic Water

Figure 9, gives pH vs. time plots for different SWB preparations. The stock solutions used for each was the same, however, preparation methods differed. The final pH value did not vary appreciably from batch to batch, with all reaching a value in close comparison with the modelled pH value of 8.04. The preparation method of each SWB iteration is described below.

SWB-1:

The first iteration involved preparing the synthetic water by combining the required stock solutions in a 1 L glass reactor and aerating with laboratory compressed air with the goal of reaching the modelled pH value of 8.04. As can be seen from Figure 9(a), the pH plateaued around 8.5 from an initial pH of 10.44 after 200 min of continued aeration. A pH of 8.57 was measured after 260 min at which time bubbling was discontinued. The solution was measured again the next morning and a pH of 8.31 was recorded. Air bubbling was continued for an additional 6 hours before a final pH measurement of 8.44 was taken. The solution was left to equilibrate over the weekend in an open beaker placed on a magnetic stirrer. The pH was measured at 8.00 and 8.06 after four and five days, respectively.
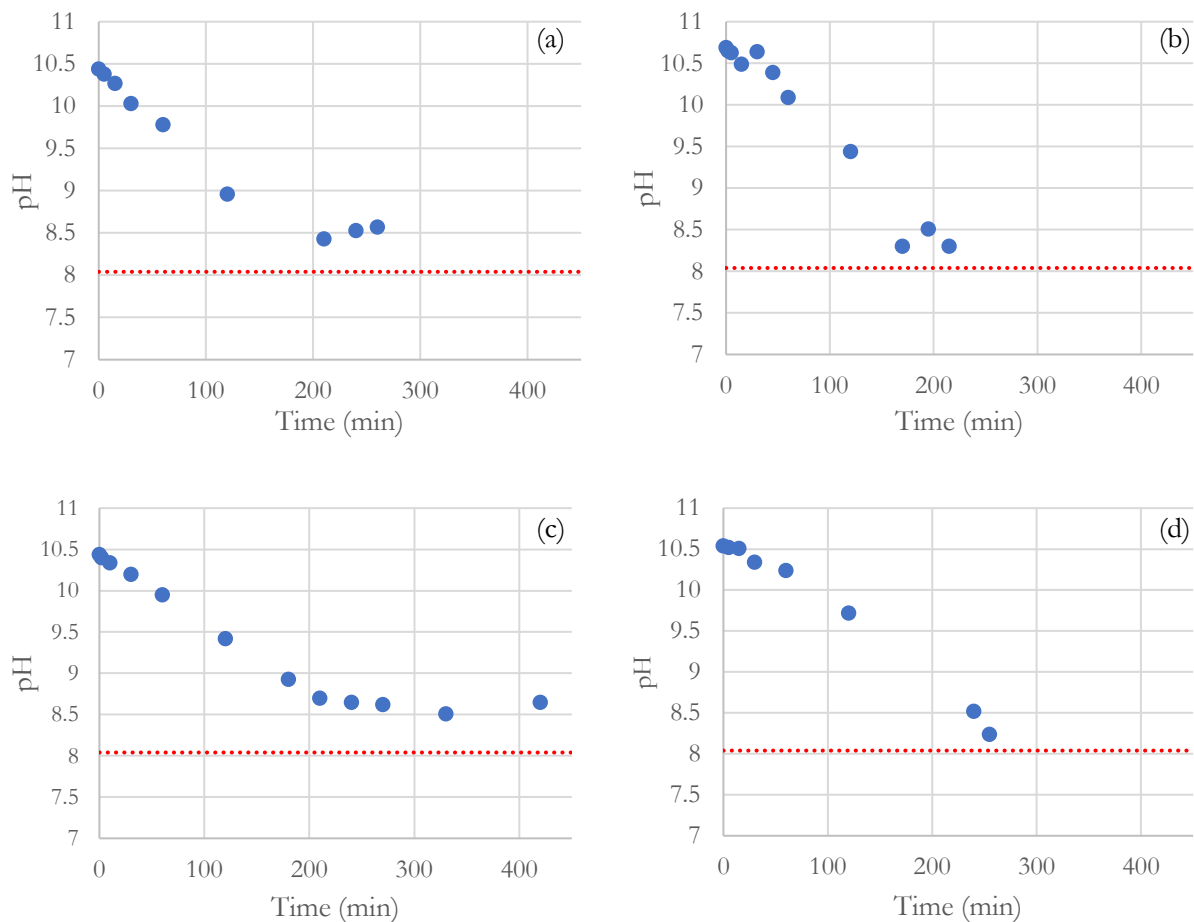
Figure 9 – pH vs. Time Plots for the Preparations of (a) SWB-1, (b) SWB-3, (c) SWB-4, and (d) SWB-5. The Trendline Represents the Modelled pH Value of 8.04.

SWB-2:

SWB-2, simply involved the preparation of the synthetic water inside a 2 L beaker which was left to equilibrate with the atmospheric CO_2. An initial pH of 10.44 was recorded with a drop to pH 10.19 after 3 hours. The pH was measured at 8.00 and 8.13 after four and five days, respectively.

SWB-3:

Given the unsuccessful attempt to aerate SWB-1 to the modelled pH value of 8.04, SWB-3 was prepared by initially bubbling the $Ca(OH)_2$ solution with compressed air followed by the addition of the other stock

solutions. The target value for the $Ca(OH)_2$ was calculated with Visual MINTEQ and a value of pH 7.81 was given. This procedure resulted in a slower initial drop in pH, however, the solution was able to reach a pH of 8.30 after 215 min. This can be seen in Figure 9(b). Air bubbling was continued briefly but due to fluctuating pH readings between 8.3 and 8.4, and an apparent plateauing, it was assumed the target pH value would not be reached and the other stock solutions were added at this stage. This resulted in a slight increase in pH, however, the pH continued to rise to a value of 8.70 after 2 hours. The pH was recorded the next morning at 8.32 and again 3 days later at pH 8.06.

SWB-4

SWB-4, Figure 9(c), was prepared in a similar manner as SWB-1, however, with a greater air bubbling time the day of preparation. Similar to SWB-1, the pH value plateaued around 8.5 after 200 min of continued bubbling. There was no significant change in pH in the 4 hours to follow and a final pH reading of 8.65 was taken. A pH value of 8.05 was recorded after 3 days.

SWB-5:

SWB-5, Figure 9(d), was prepared similar to that of SWB-3, albeit with longer air bubbling time. Once again, the pH reached a value of ~8.3 after 200+ min of continued bubbling. The $Ca(OH)_2$ solution was allowed to equilibrate with the atmospheric CO_2, and a pH of ~7.8 was reached the next morning. The other stock solutions were added later in the day resulting in a pH increase to ~8.1. A pH of 8.08 was recorded after 3 days.

SWB-6:

Given the previous results and the inability to reach the modelled pH value of 8.04 by aeration alone, it was determined CO_2 bubbling was required. The $Ca(OH)_2$ solution was prepared and bubbled with CO_2 continuously for 10 min and afterwards a pH of 5.87 was recorded. At this stage, the other stock solutions were added which resulted in a slight pH increase. To drive off the excess CO_2, air bubbling was started using the laboratory compressed air. Surprisingly, however, the modelled pH value of 8.04 was reached less than a minute

later and the pH continued to rise to 8.62 after approximately 10 minutes. This was not expected and due to the various literature citing the use of air bubbling in the preparation of synthetic water, the modelled pH value given by Visual MINTEQ, and finally the pH values of previously prepared waters left to equilibrate with the atmospheric CO_2, it was deduced that there was another issue with the system. Seeing as all previously prepared waters aerated with the laboratory compressed air plateaued around pH 8.5, a hypothesis was made that the laboratory compressed air must have a lower P_{co_2} than the atmosphere. This was confirmed in the preparation of SWB-7, where an air pump that drove in laboratory air was used for aeration.

SWB-7:

The pH vs. time plot for the final SWB preparation can be seen in Figure 10. Given the previous result, an air pump was used for the aeration of SWB-7 and a much more favourable result was attained. The $Ca(OH)_2$ solution was again prepared and bubbled with CO_2 driving the pH down to 6.23 after approximately 15 min. At this stage, the other stock solutions were added resulting in an increase to pH 6.39. CO_2 bubbling was continued to again lower the pH below 6.3. Finally, air bubbling was started and was continued for 100 min, after which time a pH value of 8.07 was recorded. This confirmed the hypothesis that the laboratory compressed air was insufficient of P_{co_2}.
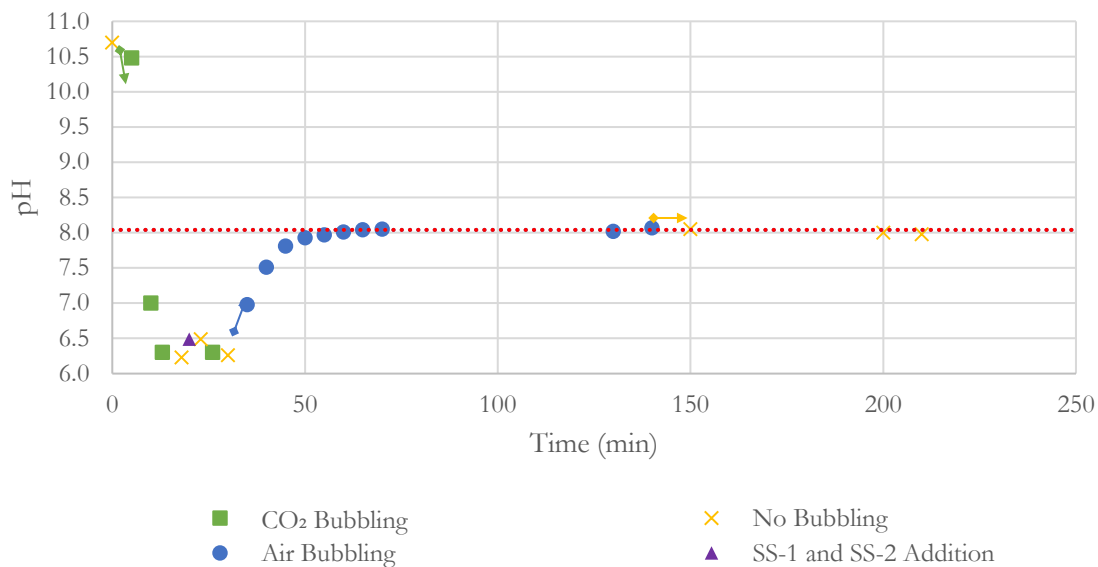
Figure 10 – pH vs. Time Plot for the Preparation of SWB-7

3.4.3. Alkalinity and Ion Analysis Results

The titration results for the SWB samples are listed in Table 7 with the total alkalinity determined using Equation 15. Each water sample was tested at least twice and the alkalinity of the sample with final pH closest to 4.5 is listed below. Unfiltered samples were also analyzed for alkalinity, however, no discernible difference between filtered and unfiltered samples was determined. Filtration, however, resulted in a slight decrease in pH.

Table 7 – Alkalinity Results SWB Samples

Sample	HCl (0.02 M) Consumed (ml)	pH		Alkalinity (mmol/L)
		Initial	Final	
SWB-1	4.21	8.04	4.51	0.84
SWB-2	4.17	8.01	4.51	0.83
SWB-3	3.79	8.06	4.51	0.76
SWB-4	3.89	7.96	4.47	0.78
SWB-5	3.84	7.98	4.50	0.77
SWB-6	3.81	7.84	4.50	0.76
SWB-7	3.72	7.94	4.48	0.74

The alkalinity results for different SWF samples are given in Table 8 with both fixed endpoint and IPT titration method values listed. The average SWF alkalinity using the fixed endpoint method was determined to be 0.76 mmol/L versus an average alkalinity of 0.73 mmol/L using the IPT method. The [HCO_3] was calculated using the advanced speciation method (Rounds, 2013) which calculates speciation from the measured sample pH and alkalinity, and calculated acid dissociation constants. The average [HCO_3^-] was also determined to be 0.73 mmol/L. The average equivalence point pH for the IPT method was determined to be at pH 4.75. Samples were again measured for alkalinity at the end of the week which resulted in slightly lower alkalinity values or no discernible difference. The final pH values for all SWF samples were recorded in close comparison to the modelled pH value of 8.04.

Table 8 – Alkalinity Results for SWF Samples

Sample	Method	Alkalinity (mmol/L)	[HCO_3^-] (mmol/L)	Equivalence Point (pH)
SWF-1	Fixed Endpoint	0.76	-	-
SWF-1	IPT	0.74	0.73	4.72
SWF-2	Fixed Endpoint	0.75	-	-
SWF-2	IPT	0.73	0.72	4.74
SWF-3	Fixed Endpoint	0.75	-	-
SWF-3	IPT	0.73	0.72	4.76
SWF-4	Fixed Endpoint	0.76	-	-
SWF-4	IPT	0.73	0.73	4.75
SWF-5	Fixed Endpoint	0.76	-	-
SWF-5	IPT	0.74	0.73	4.76

An example of a titration curve for the equivalence point determination of SWF-3 is shown in Figure 11. The equivalence point was determined using the Alkalinity Calculator (Rounds, 2012) and was found to be at pH 4.76 for this particular sample.
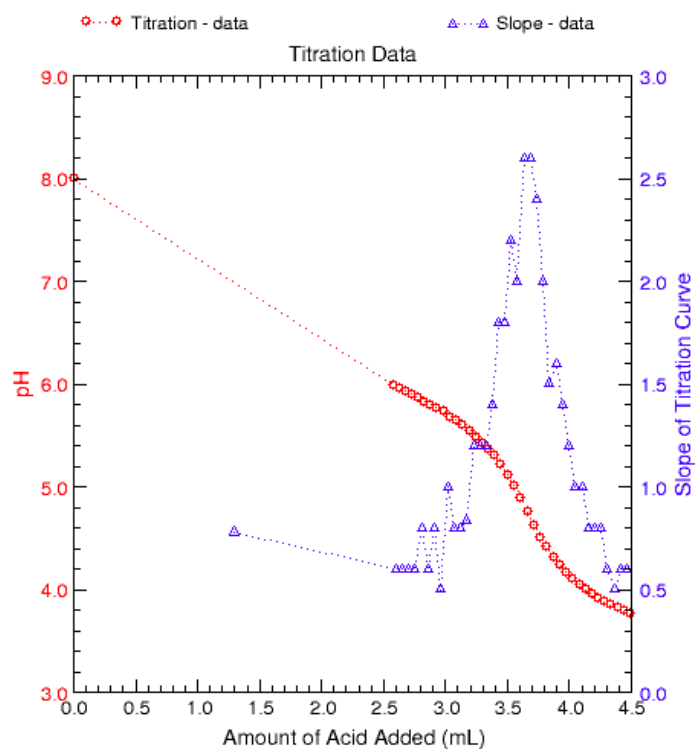
Figure 11 – Titration Curve for SWF-3 (Rounds, 2012)

The ion analysis results for SWF-1 and SWF-2 are listed in Table 9. Succeeding SWF samples were not analyzed for ion concentration; however, all samples were tested for alkalinity.

Table 9 – Ion Analysis Results for SWF-1 and SWF-2

Ion	Method	Concentration (mg/L)	
		SWF-1	SWF-2
Ca^{2+}	DIN EN ISO 11 885	8.1	8.1
K^+	DIN EN ISO 11 885	1.7	2.5
Mg^{2+}	DIN EN ISO 11 885	3.0	3.0
Na^+	DIN EN ISO 11 885	6.7	7.0
Cl^-	DIN EN ISO 10304-1	5.7	5.7
F^-	DIN EN ISO 10304-1	0.18	0.12
SO_4^{2-}	DIN EN ISO 10304-1	0.55	0.60
NO_3^-	DIN EN ISO 10304-1	0.89	0.90

3.5. Discussion and Analysis

3.5.1. Discussion of Differences

The modelled pH value of 8.04 was in good agreement with the measured pH value of all SWB and SWF samples left to equilibrate with the atmospheric CO_2. Laboratory P_{co2} was not measured, however, given that the experimental and modelled values of pH were in good agreement, it can be concluded that the standard input value for P_{co2} of 3.8 x 10^{-3} was a good approximation. However, unlike alkalinity, pH is sensitive to changes in P_{co2} as seen by the differing aeration methods, in addition, to changing pH values after filtration. Lower pH values after filtration was investigated, but as noted by Grasshoff et al. (1999), vacuum filtration can alter P_{co2} leading to different equilibrium pH values. This can also be attributed to slow pH readings.

As reported by Smith et al. (2002), the published composition of a water is usually determined analytically, therefore, the concentrations of cations and anions often do not balance exactly. Thus, taking into consideration only the constituents analyzed for our natural water source, the PBE can be calculated according to Equation 17 ([SO_4^{2-}] is given the value of 0.005 mmol/L).

$$[Na^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + [K^+] - [Cl^-] - 2[SO_4^{2-}] - [NO_3^-] - [F^-] - [HCO_3^-] \qquad (17)$$

$$[(0.283) + 2(0.207) + 2(0.118) + (0.043) - (0.203) - 2(0.005) - (0.019) - (0.006)$$
$$- (0.85)]\frac{mmol}{L} = -0.115\frac{mmol}{L}$$

This "extra" anion concentration can be attributed to the presence of titratable organic anions and other titratable anions, which can lead to an overestimation of the bicarbonate ion (Herczeg et al., 1985). By subtracting this value from the [HCO_3^-] given, and assuming an electrically neutral water, this would result in a [HCO_3^-] of 0.73 mmol/L which is in good agreement with the calculated [HCO_3^-] of 0.73 mmol/L and the expected weighed [HCO_3^-] value of 0.715 mmol/L for the SW reproduction. The measured alkalinity for all SWF samples analyzed show reproducible and consistent results, with all samples in close proximity to this expected value.

As shown, titration to 4.5 using the fixed endpoint method results in an overestimation of alkalinity in comparison to the IPT method. This resulted in an overestimation of 4.1%. This is not a significant difference, however, given lower alkalinity values resulting from milling and conditioning during the flotation process, this error can be more significant as the true equivalence point moves further away from the fixed pH value of 4.5. The equivalence point calculated at pH 4.75 for our SWF samples is a good estimate, however, equivalence point determination errors can result from a sliding of the equivalence point due to CO_2 outgassing during titration (Pearson, 1981). It should also be noted that the accuracy of the titration method is reliant on the accuracy of the pH measurement, but given the constant P_{CO_2} of the laboratory, this should give satisfactory results. Differences in alkalinity values for SWB samples can be attributed to the different stock solutions used, non-reagent grade $Ca(OH)_2$, as well as the titration method (fixed endpoint) and apparatus (25 ml burette) used for alkalinity determination. These errors are not of significance, as SWB preparation was solely to determine the methodology.

Table 10 lists the average ion concentrations of SWF samples analyzed in comparison to the expected values. Cation values show satisfactory results with the exception of K^+, while anion values show rather significant errors. However, the accuracy of the anion analysis method is in question given these expansive deviations. Specifically, the determined $[Cl^-]$ is surprising, given that the only source of chloride ions was from the addition of $MgCl_2 \cdot 6H_2O$ with $[Mg^{2+}]$ producing an error of only 3.4%. In addition, the PBE calculation of the measured values gives rise to 0.096 mmol/L greater cation concentration, which is in error of the expected electrically neutral assumption. These errors can be attributed to errors resulting from the low concentration values of the species measured, which can therefore limit the accuracy of the measurement as the detection limit is approached. These errors can also be ascribed to the different analytical methods used to determine cation and anion concentrations. Errors can also be more significant due to the small sample size of water analyzed for ion concentration.

Table 10 – SW Ion Concentration Comparison of Expected and Measured Values

Ion	Concentration (mg/L)			Error (%)
	SW Expected	SWF (Average)	Difference	
Ca^{2+}	8.3	8.1	-0.2	2.4
K^+	1.7	2.1	0.4	23.5
Mg^{2+}	2.9	3.0	0.1	3.4
Na^+	6.5	6.8	0.3	4.6
Cl^-	8.0	5.7	-2.3	28.8
F^-	0.11	0.15	0.04	36.4
SO_4^{2-}	0.48	0.57	0.09	18.8
NO_3^-	1.18	0.89	-0.29	24.6

3.6. Conclusions and Recommendations

(1) Synthetic water is an effective tool to model changes in water composition resulting from different flotation processes. The method described gives reproducible and satisfactory results. The synthetic water recipe outlined in this report can be easily modified to prepare a solution of different composition.

(2) Synthetic water should be prepared from previously prepared stock solutions of high concentration and salt compatibility. Care should be taken to avoid surpassing the solubility limit of the added salts and/or oversaturation with respect to insoluble minerals. The latter can be confirmed using a chemical equilibria software such as Visual MINTEQ.

(3) CO_2 bubbling is an efficient way to speed up the kinetics of hydroxide conversion and to promote dissolution of calcium carbonate. Aeration is required to equilibrate the solution with the atmospheric CO_2, with care taken to assure any air used is of matching atmospheric P_{CO_2}.

(4) 25 L of synthetic water can be prepared in less than half a day from previously prepared stock solutions and should be replaced at least weekly. A pH value of ~8.0 is reached for this particular synthetic water recipe which is in good agreement with the modelled pH value of 8.04.

(5) Alkalinity values calculated using the IPT method show satisfactory agreement with the expected bicarbonate concentration. Titration using the fixed endpoint method to pH ~4.5 resulted in an overestimation of alkalinity and, therefore, is not recommended for alkalinity determination of low alkaline natural water.

(6) Differences in bicarbonate concentration between the target water and synthetic water can be attributed to the presence of other titratable anions and/or resulting from seasonal variation.

(7) Ion analysis produced conflicting results with the anion concentration of SWF samples producing significant errors. This is believed to be attributed to errors resulting from the limited accuracy of the measurement as the concentration of certain species approached the detection limit of the apparatus.

Acknowledgements

4. BENEFITS GAINED

It is with regret that my internship ended on August 31, 2017, however, over the four-month work period, I benefitted greatly both professionally and personally. I was able to apply the skills and knowledge gained during my studies, meanwhile, picking up new skills which will ultimately allow me to become a better engineer. This included learning how to apply the engineering approach in practice and improving my technical skills in the laboratory. Furthermore, I considerably strengthened my presentation skills and the ability to convey my ideas and findings to others. In closing, I gained a great deal from this internship and it made all the difference in my academic journey this year and the years to come.

5. SAFETY TRAINING AND PRACTICES

The Helmholtz-Zentrum Dresden-Rossendorf places a great emphasis on good safety practices and procedures. All new employees are given a general safety talk followed by a mandatory safety seminar giving a detailed overview of the safety policy and associated health risks and emergency response procedures. Personal safety equipment (PSE) is used at all times in the laboratory, consisting of a lab coat and safety googles. Additional personal safety equipment such as gloves and respirators are used as needed. All labs are fitted with fume hoods, eye wash stations, and safety showers. Safety Data Sheets (SDS) are available for all reagents. All solutions are labeled and stored appropriately and reagents outside of their original bottles are fitted with the appropriate label. Any broken glass is placed in the appropriate container. It is mandatory to have at least one senior coworker available on the floor when using the laboratory. Any accidents and/or emergencies must be reported immediately and proper precautions must be taken at all times.

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