

Influence of Magnetic Fields on Calcium Carbonate Scaling in Aqueous Solutions at 150°C and 1 Bar

Ammar Al Helal¹, Adam Soames¹, Rolf Gubner¹, Stefan Iglauer², Ahmed Barifcani¹

1. Chemical Engineering Department, Curtin University, Perth W.A., Australia
2. Petroleum Engineering Department, Curtin University, Perth W.A., Australia

Abstract

The experiments performed as a part of this study were conducted to evaluate the effect of magnetic field treatment upon the scale forming tendency of brine solution composed primarily of calcium bicarbonate ions. The reported results were generated using a Dynamic Scale Loop system with the brine solution exposed to a magnetic field generated by a 6480 Gauss magnet of grade N45SH in a diametrical orientation for 2.5 seconds. Following magnetic exposure, the brine solution was exposed to an elevated temperature 150°C at 1bar to promote the formation of scale within a capillary tube. The extent of scaling was measured by recording the differential pressure across the tube as scaling proceeded.

Three important conclusions regarding the effect of magnetic field treatment upon scale formation in calcium bicarbonate solutions were reached. Firstly, the ratio of calcium to bicarbonate plays a key role in determining how magnetic fields influence scale formation, whether promoting or inhibiting it. Solutions containing high concentrations of the bicarbonate, or equal concentrations of the bicarbonate and calcium species showed inhibited scale formation following magnetic exposure. Secondly, the electrical conductivity of the calcium carbonate solution was noticeably impacted by the exposure to the magnetic field through manipulation of the ionic hydration shell and may also provide a measure of the extent of scale formation. Finally, the application of magnetic field treatment for scale inhibition may provide an alternative eco-friendly scale inhibition strategy in place of traditional chemical scale inhibitors.

Keywords: Scaling; Scale Inhibition; Diametrically Magnetic Treatment; Dynamic Scale Loop; DSL

1.0 Introduction

Inorganic mineral deposits, predominately carbonate minerals, are often problematic in industrial processes including oil and gas production, thermal power plants, nuclear power stations, paper production, and desalination processing facilities [1-3]. Carbonate minerals in the form of calcite deposition, is thus a subject of vital interest due to its side effects in industrial processing, which has been a persistent problem in maintaining flow assurance and continuous operation [4]. Several investigations have been performed by researchers to evaluate suitable techniques that may reduce the scaling issues faced in the oil and gas industry [2, 5-7].

Typically, Chemical Scale Inhibitors (CSIs) are an effective method to control inorganic deposition problems [8-11]. However, the addition of CSIs has been shown to impact system chemistry and may also be expensive to perform [11]. Furthermore, the applicability and the performance of CSI is dependent on several parameters such as toxicity, solubility, thermal stability, hydrolytic stability, degradation level, and minimum inhibitory concentration (MIC) [5, 10, 12]. Where the latter, represents the minimum effective concentration of CSI to prevent scaling in different industrial processes [2, 5, 10]. Despite some efforts to rank different scale inhibitors by evaluating their ability to inhibit scale formation at various conditions, a final comparison of their performance is difficult [2]. Essentially, it has been established that there are two primary laboratory methods to evaluate scale inhibitor performance per the National Association of Corrosion Engineers (NACE) standard testing method; Dynamic Scale Loop technique (DSL) and the jar test technique (static) [5, 13, 14].

The DSL method often gives rise to a different performance ranking than tests performed using the static jar test [5, 15, 16]. These differences in ranking are often attributed to the discrepancies in the response time of each technique [6, 17]. For instance, the efficiency of scale inhibitors evaluated using the DSL technique are determined by comparing the time required to impede a thin steel tube in the presence of scale inhibitors to the time needed to obstruct the same narrow steel tube without scale inhibitors [18, 19]. Conversely, the efficiency of scale inhibitors in the jar technique is determined by comparing the time required to minimize the formation of scale in the presence of scale inhibitors in comparison to a blank test [15, 18, 19].

In a previous publication by Bazin, Kohler and Zaitoun [5], it was determined that the DSL test is more reliable for evaluating anti-nucleation inhibitors while the crystallization inhibitors are often tested using the static method [16, 20, 21]. As a result, both techniques have limited boundaries to assess the performance of different scale inhibitors [22]. Bazin, Kohler and Zaitoun [5] have also pointed out that the residence time in the static test is longer than DSL

test, which is an advantage to the latter technique [12]. Recent reports indicate that the DSL technique could provide researchers with sufficient data to understand the kinetic and thermodynamic behavior of mineral solubility in moderate conditions with varying flow rates, pH, temperature, pressure and total dissolved solids [6, 17, 23, 24].

Having reviewed the literature on both techniques to evaluate the performance of chemical inhibitors, we have not observed their use to assess the performance of non-chemical alternatives which may contribute to reducing scale formation. For example, one of the most important non-chemical alternatives currently controversial is the magnetic treatments that unfortunately were not employed properly to confirm their effectiveness towards the deposition. Positive results generated using traditional anti-scale magnetic treatment (AMT) methods have been reported by various authors in recent years [25-30]. Zaidi, Sohaili, Muda and Sillanpää [31] concluded that the implementation of a magnetic field can promote the physical performance of solid-liquid separation by improved gathering of the colloidal particles through manipulation of particle arrangement. Fathi, Mohamed, Claude, Maurin and Mohamed [32] found that AMT can enhance the precipitation of CaCO_3 in aqueous solution by controlling the solution pH, flow rate and time of exposure. Furthermore, Fathi, Mohamed, Claude, Maurin and Mohamed [32] observed that AMT affected the mineral ions involved in the formation of CaCO_3 and suggested that CaCO_3 is not required to be present for the magnetic field treatment to influence its scale formation tendencies. Baker and Judd [11] reviewed in detail the advantages and the disadvantages of AMT when applied during small-scale water treatment. They presented several positive results that indicate the aggregation of particles was enhanced, and the size of hydrophilic crystals were observed to be greater than usual [11].

The research performed by Baker and Judd [11] also stated that the AMT technique was successful when applied to thermal circulating processes such as reboilers and heat exchangers through reduced carbonate scaling during operation. It has also been established that AMT can lead to large savings in cleaning, power consumption, time, maintenance cost and unexpected shutdowns within water-based applications such as water treatment, paper production processes and within the oil and gas industry [11, 21, 33, 34].

In addition, Higashitani, Kage, Katamura, Imai and Hatade [29] concluded that the growth of CaCO_3 particles was accelerated at high magnetic field densities if exposed for more than 10 minutes. Higashitani, Kage, Katamura, Imai and Hatade [29] attributed the effect of magnetic exposure upon CaCO_3 growth behavior to the effect of the applied magnetic field solely upon the bicarbonate species prior to mixing with calcium ions. The results of Higashitani, Kage,

Katamura, Imai and Hatade [29] highlighted the different response of the cationic (calcium) and anionic (bicarbonate) species to magnetic exposure. A similar finding was concluded by Baker and Judd [11] who stated that magnetic exposure primarily effects the anion component of the scale forming compound.

Furthermore, Baker and Judd [11] have stated that permanent magnets can be classified into four divisions with each division utilising different orientations of AMT (orthogonal or parallel) to the direction of flow, refer to Figure 1-1 [11, 31, 35]. They further suggested that the different magnet orientations may provide different responses in terms how they influence scale formation. Zaidi, Sohaili, Muda and Sillanpää [31] and Alimi, Tlili, Amor, Gabrielli and Maurin [3] reported that it is preferable to use permanent magnets for water treatment because they are capable of generating a uniform magnetic field. As well as the ease of manufacturing magnets with a high magnetic strength such as Neodymium N45SH which can thermally withstand temperatures of up to 150°C. This is in addition to the possibility of designing different shapes, dimensions and orientations such as axially or diametrically magnetized [11].

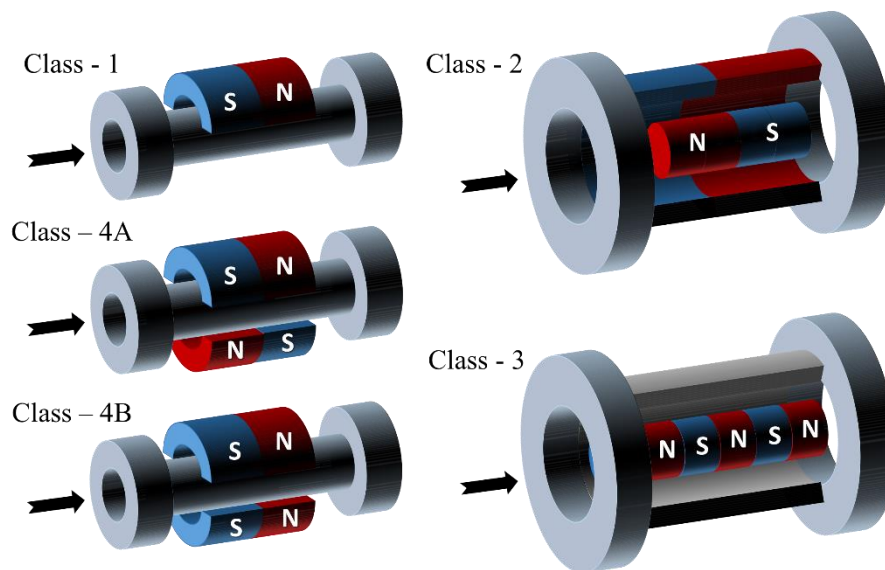


Figure 1-1 - Recommended magnetic field orientations across the fluid flow in pipelines,
 Class 4A is diametrically magnetized and Class 4B is axially magnetized [11].

On the other hand, it has been reported by Busch and Busch [34] and Baker and Judd [11] that the AMT technique, when applied to industrial water treatment, was ineffective. However, the precise cause(s) of failure are yet to be fully determined [36, 37]. Furthermore, other sources of literature have criticized the AMT technique due to the lack of systematic lab evidence [21,

37]. Thus the efficiency of AMT for inhibiting scale formation is still disputed and a precise explanation of how AMT influences the formation of scale is unclear [32].

The purpose of this study is to evaluate the use of the DSL technique in the presence of magnetic fields (Neodymium Magnet N45SH) to determine its impact on the scale formation. The DSL technology has been established as a novel method for evaluating chemical scaling inhibitor inside capillary tubes, but has yet to be applied in determining the effect of magnetic field strength and magnetic direction (diametrically magnetized) upon scale formation. Furthermore, the influence of atmospheric pressure and moderate temperature (150°C) upon mineral solutions has not been previously investigated when using the DSL and diametrically magnetized magnet techniques together. Within this study, the DSL technology has been utilized to evaluate the validity of non-chemical treatment against calcium carbonate scale formation as it is unclear to what extent non-chemical treatments such as magnetic fields contribute to scale formation when using the DSL technique.

2.0 Magnetic Field Concepts

To understand the application of magnetic fields in water treatment, there are three main concepts that must be considered as discussed by Zaidi, Sohaili, Muda and Sillanpää [31], Okada, Ozaki and Matijević [38], Oshitani, Yamada, Miyahara and Higashitani [39] and Higashitani, Iseri, Okuhara, Kage and Hatade [40]. These concepts can be categorized as follows: magnetism and the effects of magnetic fields [41], magnetic gradient [39], and magnetic memory [39]. The first factor describes the relationship between positive and negative charges of particles, ions and molecules and their response to magnetic fields [39]. Meanwhile, molecules can be divided into two categories, polar such as water and non-polar such as fats, oil, and petrol/gasoline [41-43]. The type of molecules, whether polar or non-polar will dictate how said molecules would respond when exposed to a high-intensity magnetic field.

Göllei [44] and Zaidi, Sohaili, Muda and Sillanpää [31] claimed that within non polar molecules, the proton and electron centres of gravity act around the same point . This central coincide leads to continuous random movement in the absence of a magnetic field, and thus the molecules are less susceptible to coagulation [38, 45, 46]. However, Zaidi, Sohaili, Muda and Sillanpää [31] reported that if a non-polar molecule system is exposed to a magnetic field generated by an electro-magnet, the molecules will adopt a less random movement pattern, and the molecules will rearrange according to the direction of the magnetic flux, refer to Figure

2-1. As the non-polar molecules travel through the electro-magnetic field, an induced dipole moment is generated. This rearrangement will promote the coagulation of the molecules after magnetic field exposure [38, 45]. However, in contrast to non-polar molecules, prior to being exposed to a magnetic field, polar molecules exhibit a more random arrangement. Due to the random arrangement of polar molecules in combination with the repulsion caused by the similarly charged ends of the surrounding particles, coagulation is unlikely to occur [38]. In a similar manner to non-polar molecules, the application of a strong magnetic field can result in the rearrangement of the polar molecules to promote molecular coagulation [38, 46].

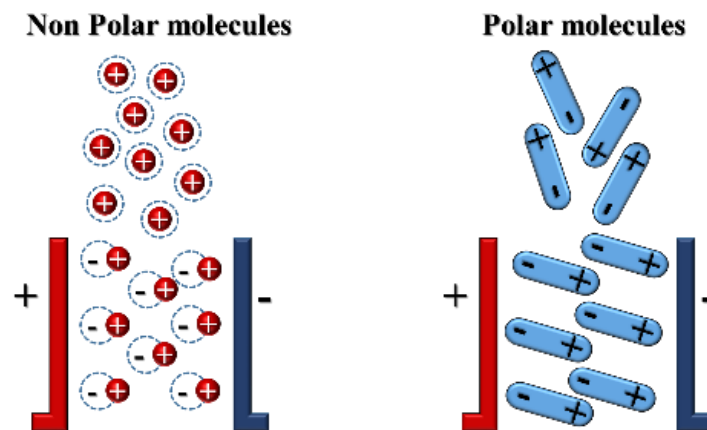


Figure 2-1 – Structure of non-polar and polar molecules and their arrangement as they pass through an electro-magnetic field

Furthermore, as a charged particle travels through a magnetic field, the particle will experience a force (the Lorentz force). The Lorentz force acts upon a charged particle according to the ‘right hand rule’ and indicates that a charged particle travelling through a magnetic field will undergo a deviation in its trajectory perpendicular to the magnetic field and axis of movement [47, 48]. The extent of the force exerted upon a charge particle can be estimated through Equation 1 and is dependent upon the particles charge, whether positive or negative, its velocity as it travels through the magnetic field and the strength of the magnetic field itself [49]. As a particle can be either negatively or positively charged, the direction of the applied force will produce a separation effect upon oppositely charged particles as per Figure 2-2 [31].

$$\vec{F} = q \cdot \vec{v} \cdot \vec{B} \quad (1)$$

Where the \vec{F} represents the Lorentz force, which is a function of the electric charge of the particle q in Coulomb, instantaneous velocity \vec{v} in $\frac{m}{s}$ and magnetic field \vec{B} in Tesla.

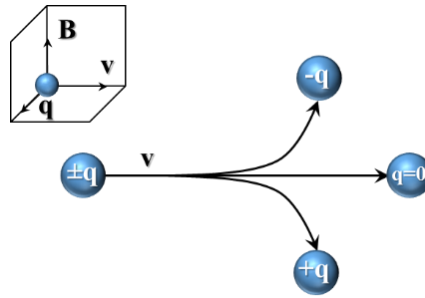


Figure 2-2 - Lorentz force and the right-hand rule movement of charged molecules

The second concept required to understand the potential effects of magnetic field exposure upon scale formation, is the concept of magnetic flux density. The flux density of a magnet is dependent on several factors including, the type, shape and the source of the magnetic field whether electric or a permanent magnet [31, 50]. In addition, the materials used to make a magnet such as Neodymium, Samarium, Alnico and Ceramic represent a key factor in determining a magnet's magnetic flux intensity. For example, Neodymium type magnets have a higher flux density when compared to the other types of the same magnetic field strength. As such, the magnetic flux density of a magnet is often more important than its strength in determining how they will influence particles.

Oshitani, Yamada, Miyahara and Higashitani [39] reported that when the flux density of a magnetic field is uniform, the exposed molecules will tend to rearrange themselves according to the direction of the magnetic field, with the separation of the molecules becoming more likely. Oshitani, Yamada, Miyahara and Higashitani [39] have reported that the influence of magnetic fields upon smaller molecules is greater than larger molecules. As a result, Vick [45] claimed that the alignment of small sized molecules tends to orientate more according to the direction of the applied magnetic field than larger molecules. Furthermore, when exposed to a magnetic field of greater flux density, the resulting Lorentz's force generated upon that particle will be greater than that produced by magnetic fields of lesser density. [47, 48]. The first and second concepts discussed are critical to understanding the relationship between magnet fields and the behavior of exposed molecules.

The final concept is related to the theory of memory effect, which defines the relationship between the magnetic exposure intensity and retention time. In other words, to what extent the effects of magnetic exposure remain active on magnetized particles after magnetic exposure has concluded [39]. It is important to maintain the influence of magnetic fields upon the exposed particles for as long as possible to ensure maximum impact.

3.0 Experimental Methodology

3.1. Chemicals and Equipment Used

3.1.1. Brine Solutions

Three water systems were utilized in these investigations. Each set contained a different initial concentration ratio of calcium to bicarbonate ions. Where set one contained high bicarbonate ion (high HCO_3^- , approximately 3000 ppm) with low Calcium ion (Ca^{2+} , approximately 110 ppm). Set two contained high Calcium ions (high Ca^{2+} , approximately 8200 ppm) with low bicarbonate ion (HCO_3^- , approximately 150 ppm), and lastly, set three contained equal amounts of calcium and bicarbonate ions ($\text{Ca}^{2+} = \text{HCO}_3^-$, approximately 700 ppm). The ionic charges of all solutions were balanced by addition of sodium chloride, and the ionic strengths were calculated for each solution, as shown in Table 1. These three sets were utilized in this study to simulate brine water at a different ionic strengths and different saturation index levels to investigate the influence of AMT upon the Ca^{2+} and HCO_3^- ions.

3.1.2. Chemicals Used

The chemical makeup of the brine solutions consisted of calcium chloride dihydrate powder (Scharlau reagent grade ACS, >99%), magnesium chloride hexahydrate powder (Chem-Supply reagent grade, >99%), sodium chloride powder (chem-supply reagent grade, 99.7%), sodium hydrogen carbonate powder Chem-Supply reagent grade, 99.7%), ethylene diamine tetraacetic acid disodium salt dihydrate (EDTA solution) (chem-supply reagent grade, 0.1 Molar), citric acid powder (ROWE Scientific PTY LTD reagent grade, >98%). The relevant chemical compositions of the brine solutions are listed in Table 1.

Table 1 - Brine water concentrations for sets 1, 2 and 3

Set-1: High Bicarbonate Low Calcium			
Ions	Bicarbonate (mg/L)	Calcium (mg/L)	Mixed Solution at DSL (mg/L)
Na^+	12257	12257	12257
Mg^{2+}	-	100	50
Ca^{2+}	-	220	110
Cl^-	15416	19583	17499.5
HCO_3^-	6000	-	3000
pH	8.20	6.36	pH= 7.16*, pH= 6.88**
		Ionic Strength, mole/L	0.54***

Set-2: Low Bicarbonate High Calcium

Ions	Bicarbonate (mg/L)	Calcium (mg/L)	Mixed Solution at DSL (mg/L)
Na ⁺	2000	2000	2000
Mg ²⁺	-	100	50
Ca ²⁺	-	16400	8300
Cl ⁻	2910	32392	17651
HCO ₃ ⁻	300	-	150
pH	8.19	6.36	pH= 7.16*, pH= 5.85**
Ionic Strength, mole/L			0.707***

Set-3: Equal Bicarbonate and Calcium

Ions	Bicarbonate (mg/L)	Calcium (mg/L)	Mixed Solution at DSL (mg/L)
Na ⁺	10600	10600	10600
Mg ²⁺	-	100	50
Ca ²⁺	-	1400	700
Cl ⁻	15533.4	19116	17325
HCO ₃ ⁻	1400	-	700
pH	8.20	6.34	pH= 7.16*, pH= 5.6**
Ionic Strength, mole/L			0.517***

* Initial pH of mixed solution before injection to DSL.

** Final pH of the mixed solution after injection to DSL.

*** Aqion software was used to calculate the required parameters such as ionic strength.

3.2. Cleaning Procedure

The cleaning method is an important step to keep the apparatus clean and to ensure accurate test results. Firstly, the capillary tubes and tubing lines were cleaned with citric acid 20 gm/L to dissolve any depositions followed by 8 gm/L of Ethylene Diamine Tetraacetic Acid Disodium salt Dihydrate (EDTA disodium, pH≈8) to react with the remaining divalent ions such as calcium and magnesium. Then the DSL tubes were flushed with deionized water before performing the proceeding tests. Furthermore, before starting any experiment, deionized water was injected into the DSL system for at least 30 minutes to stabilize all the sensors and detectors such as pH, electrical conductivity, thermocouples and the pressure sensor. The extensive cleaning procedure ensures minimal contamination therefore increasing the repeatability and accuracy of testing.

3.3. Magnet Field Unit

An Neodymium magnet of grade N45SH was utilised within this study for its high residual flux density and potential to influence scale formation behavior. The class four-A magnet

orientation with diametrically magnetized direction illustrated by Figure 1-1 was selected due to its flexibility in installation and was installed around the mixing tubing lines before exposing the calcium and bicarbonate fluids to the heating chamber as per Figure 3-2. The ring shape of the class four-A magnet orientation incorporates a small hole through the center generating a concentrated magnetic field at the center of the magnet as shown in Figure 3-1. The field strength of the magnet was measured in the center of the magnet by using a Koshava Tesla meter supplied by wutronic/Germany, with the magnet specifications outlined Table 2.

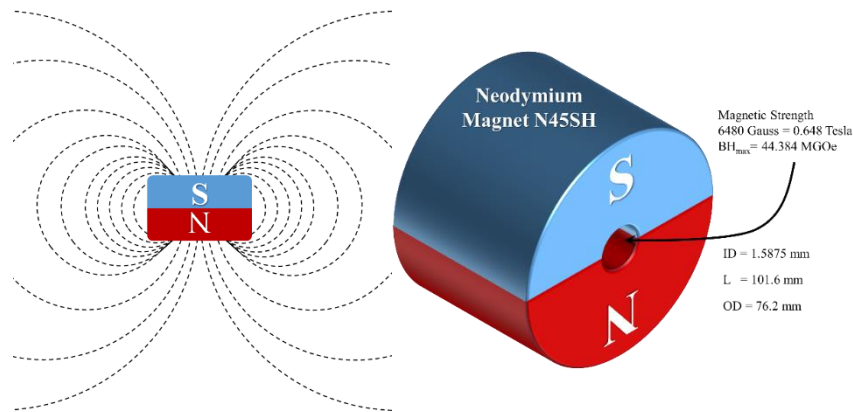


Figure 3-1 - Dimensions and shape of the diametrically magnetize magnet and depiction of the diametrical magnetic field.

Table 2 - Magnet specifications and dimensions.

Property	Specification
Magnet Dimensions	76.2 mm OD, 1.5875 mm ID, 101.6 mm Thickness
Materials	NdFeB
Grade	N45SH
Plating/Coating	Ni-Cu-Ni (Nickle)
Magnetization Direction	Diametrically magnetized
Gross weight	8 kg
Max operating temperature	150°C
Residual Flux Density $B_{r_{max}}$	13499 Gauss
The Maximum Energy Product BH_{max}	44.384 Megagauss Oersted (MGOe)
Magnetic field strength at the center	6480 Gauss at 15.4 mm inside the magnet

3.4. Experimental Setup

The experiments within this study were conducted to evaluate the scaling tendency of a solution containing bicarbonate and calcium in the presence of a diametrically magnetic field (Figure 1-1 and Figure 3-1) using the DSL technique. To measure the influence of the applied magnetic field upon the tendency of the solution to form scale, the DSL system measures the pressure increase across an internal capillary tube using pressure sensors located at the tubes inlet and

outlet with accuracy of ± 0.01 bar. An increase in pressure across the capillary tube is indicative of scale formation as the flow of liquid is impeded. To assess the effect of the magnetic field on scale formation, the pressure across the tube was measured until complete blockage of the tube occurred as indicated by a sharp increase in pressure recorded by the DSL system. The time taken for each solution to achieve complete blockage of the capillary tube was used to measure the tendency of the solution to form scale. Overall, eight sets of blank (no magnetic exposure) and magnetically exposed trials were conducted for each brine composition to ensure accuracy and repeatability of results.

The calcium and bicarbonate solutions were injected into the DSL system by using two high-performance liquid chromatography pumps from PSL technology (one for the bicarbonate fluid and one for the calcium fluid). The total injection rate for the two solutions was maintained at 5 ml/min. The laboratory DSL apparatus is illustrated in detail in Figure 3-2 with specifications listed in Table 3. The DSL device contains two individual coils with the first used to provide mixing of the solution and the second exposed to a high temperature within a heat chamber to promote the growth of scale (refer to Table 3 for coil dimensions). Following mixing within the first coil, the solution is then passed through the centre of a neodymium magnet for a total of 2.5 seconds with a magnetic field strength of approximately 6480 Gauss at the centre and maximum energy product BH_{max} around 44.384 MGOe as shown in Figure 3-1 and Table 2.

After exposure to the magnetic field, the solution enters the second coil located inside an electrical heating chamber controlled using a digital interface. The temperature of the heating chamber was maintained at 150°C ($\pm 1^{\circ}\text{C}$) throughout testing. Furthermore, the operating conditions such as flow rate and the temperature were controlled by using the *winDSL* software. A back pressure regulator was connected to the outlet line of the testing coil to maintain the pressure across the capillary tube. A GMH 5550 pH meter and GMH 5450 electrical conductivity (EC) meter were connected to the discharge line to monitor the change in pH and EC level after magnetic exposure, as per Table 3 and Figure 3-2.

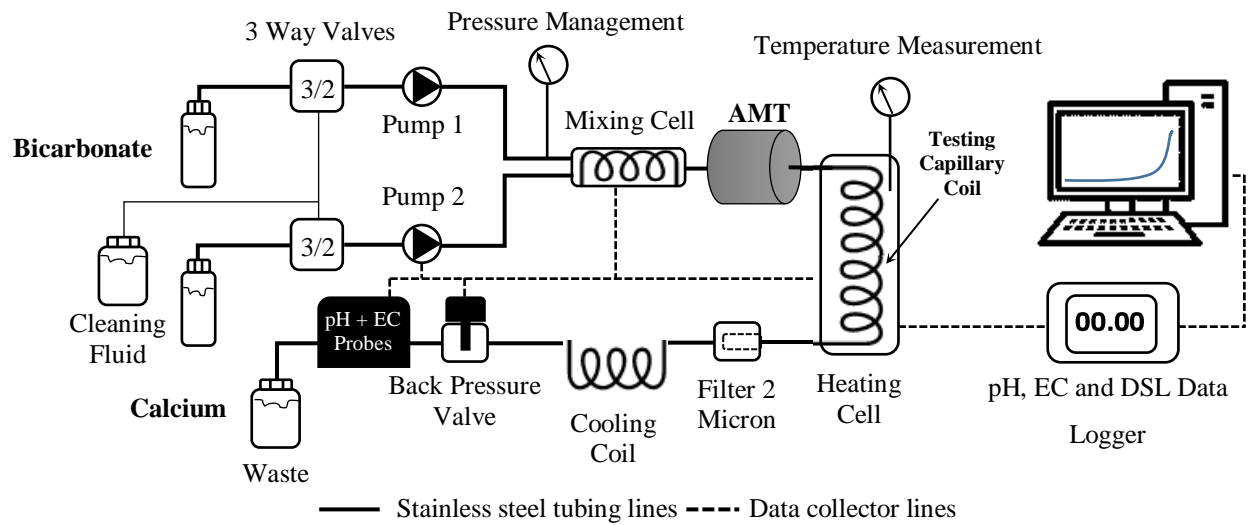


Figure 3-2 - Schematic of the dynamic flow loop.

Table 3 - Dynamic Scale Loop specifications.

Component	Specifications	Notes
HPLC pumps	0.1 – 5 ml/min, ± 0.01 ml/min	Data-logger
Mixing Coil	1 m Length, 3.171 mm OD and 1.01 mm ID	Stainless steel 316
Test Coil	1 m Length, 1.411 mm OD and 0.76 mm ID	Stainless steel 316
Back Pressure Valve	0 – 172 bar, ± 0.01 bar	Data-logger
Pressure Range	1 bar to 172 bar	Regulating
Heating Chamber	+30 to +250°C, ± 0.1 °C	Regulating
pH meter	1-14	Data-logger
Electrical Conductivity meter	0 – 1000 mS/cm, ± 0.1 %	Data-logger
Micro Filter	2 micron	Stainless steel

4.0 Results and Discussion

4.1. Concentrated HCO_3^- Solution

The results generated using the high concentration bicarbonate solution have demonstrated that exposure to a magnetic field can inhibit the formation of calcium carbonate scale. These results were obtained after exposing the brine solution to the magnetic field with a field strength of 6480 Gauss and diametrically magnetized magnet type for 2.5 seconds and comparing the results to a ‘blank’ test where no magnetic exposure occurred. From **Error! Reference source not found.**, the responses of concentrated bicarbonate solution in terms of pressure change versus time has been plotted for the solutions exposed to a magnetic field and the blank tests. In total, eight trials were conducted for both the exposed and blank trials with the average result

plotted as shown in **Error! Reference source not found.**, error bars have been included indicating one standard deviation of all eight trials away from the average result.

It can be clearly observed that the exposure to the magnetic field has generated an inhibition effect upon the tendency of the bicarbonate solution to form scale in comparison to the non-exposed blank test solution. The sharp increase in pressure observed in both cases is indicative of the capillary tube becoming blocked due to the formation of scale. It can also be noted that the time required for a full capillary tube blockage under magnetic exposure was 8.5 minutes. On the other hand, the time needed to block the same capillary tube under the same conditions but without exposure to the magnetic field was 6.0 minutes. This result means that magnetic field treatment has effectively reduced the rate of scale formation of the bicarbonate solution.

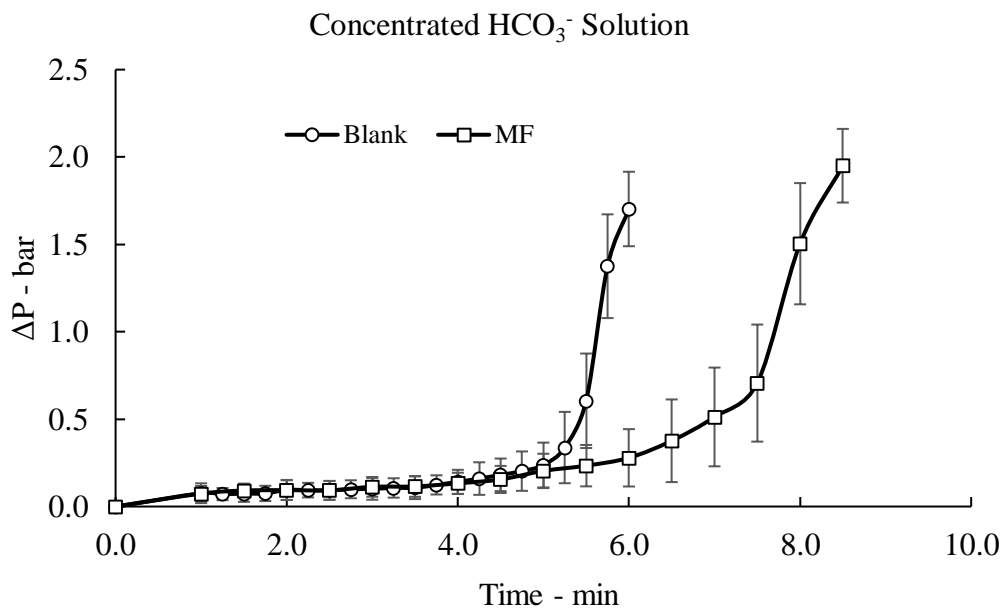


Figure 4-1 Effect of magnet field exposure upon the tendency of high bicarbonate solution to form scale

The reduced scaling tendency of the magnetically exposed solution illustrated by **Error! Reference source not found.** can be explained by the intermolecular separation of the calcium and bicarbonate ions generated by the Lorentz force as they travel through the magnetic field. **Error! Reference source not found.** illustrates the applied magnetic field within the capillary tube perpendicular to the fluid flow containing the calcium and bicarbonate ions. As the fluid passes through the magnetic field, the positive and negatively charged ions are attracted to opposite sides of the capillary tube due to the equal, but opposite Lorentz force applied and are thus separated. As the separated ions (calcium and bicarbonate) enter the capillary tube under

elevated temperature, the tendency of the solution to form scale is inhibited. The extent to which the oppositely charged ionic species remain separated is referred to as the memory effect, with the extent of separation decreasing as time progresses following magnetic exposure.

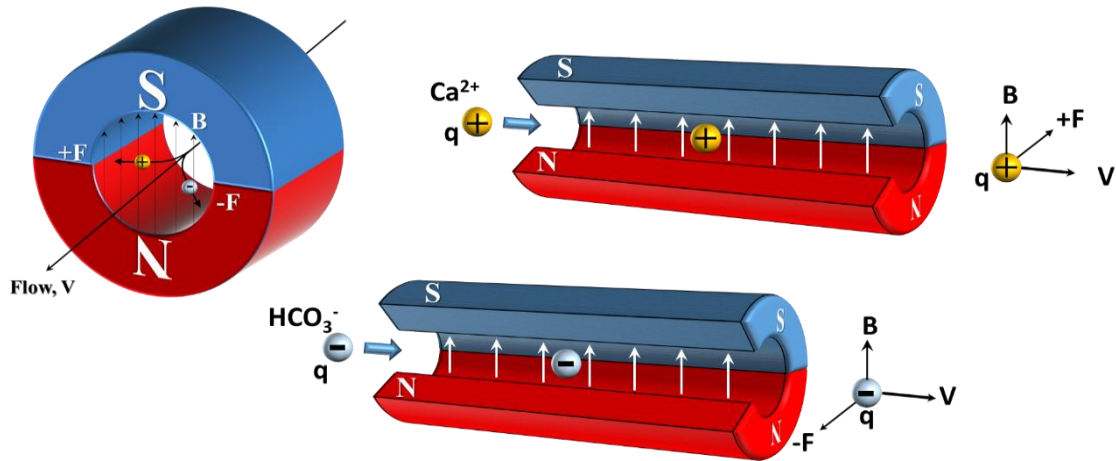


Figure 4-2 Influence of magnetic fields on charged particles

Another interesting result has been observed as shown by Figure 4-3 where the measured electrical conductivity deviated between the control and exposed solutions. A slight change in the electrical conductivity readings were observed over the range of 0 to 5 minutes where the bicarbonate solution experienced a significant decrease in the conductivity when exposed to magnetic field. This experimental result is in line with the findings of Hasaani, Hadi and Rasheed [51] who observed a similar reduction in electrical conductivity measurement in calcium-bicarbonate solution following exposure to a magnetic field. Furthermore, whilst evaluating the effect of magnetic field exposure on scale formation, Szczes, Chibowski, Holysz and Rafalski [52], Holysz, Szczes and Chibowski [53] and Marcus [54] concluded that the hydration shell thickness of the bicarbonate and calcium ions are subject to manipulation by magnetic fields leading to changes in electrical conductivity measurement. Overall, the exposure of the ions to the magnetic field has increased the hydration shell thickness of the bicarbonate ions causing the reduced electrical conductivity measurements experienced within this test. The effects of magnetic field exposure upon the hydration shell of the ionic species is further discussed in Section 0.

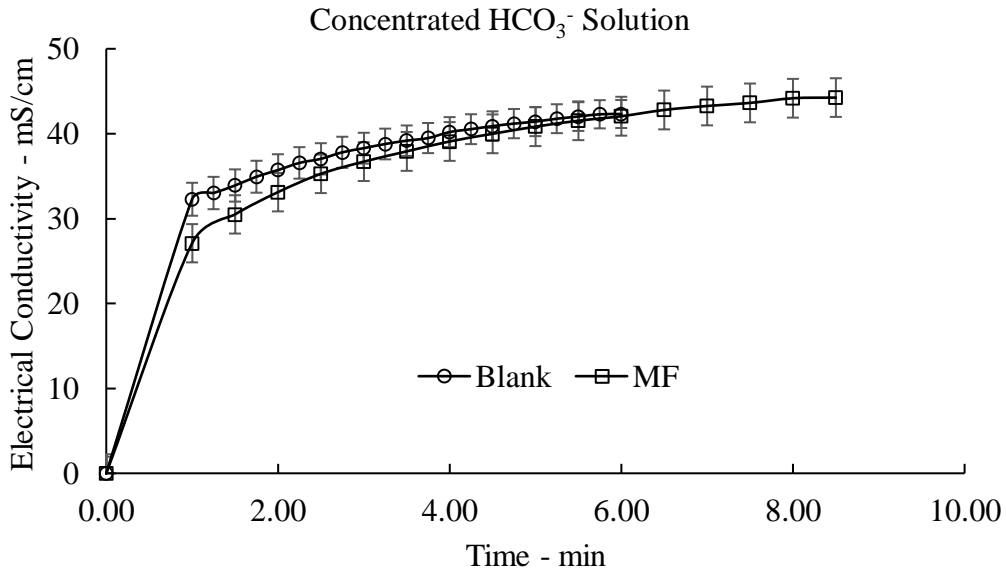


Figure 4-3 - Effect of magnet field exposure upon electrical conductivity of high concentration bicarbonate solution

Additionally, if we compare the electrical conductivity response measured during the test with the change in pressure with time as illustrated in **Error! Reference source not found.**, a clear relationship between the electrical conductivity and extent of scale formation is evident. As the formation of scale proceeds, the electrical conductivity measured at the outlet of the system gradually increases until it reaches the maximum electrical conductivity at the point of blockage within the tube. The initial spike in electrical conductivity experienced over the first minute of the experiment represents the initial mixing within the system and response of the electrical conductivity meter as it is first exposed to the solution. It can therefore be concluded that electrical conductivity may provide a measure of scale formation within pipelines as a clear increase in electrical conductivity occurs in response to scale formation within the capillary tube [53, 55].

As the formation of CaCO_3 scale within the system proceeded during testing, a minor decrease in pH at the outlet of the system was observed as shown in

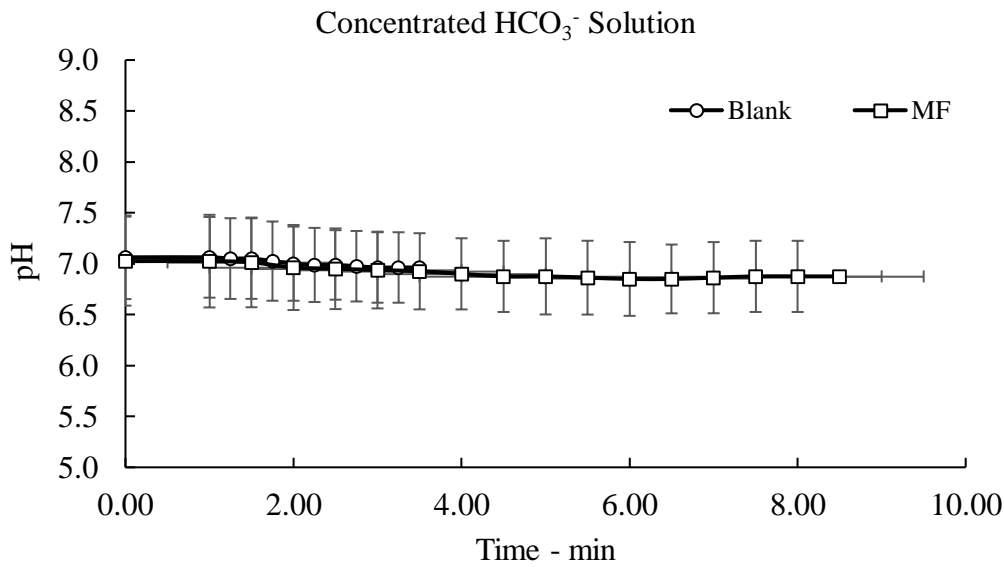


Figure 4-4. The reaction of calcium and bicarbonate ions to form scale produces a free hydrogen ion and as such, a reduction in pH can be expected. Of the tests conducted, little to no difference in pH of the exposed and non-exposed solutions is evident indicating there is no impact upon pH due to magnetic exposure.

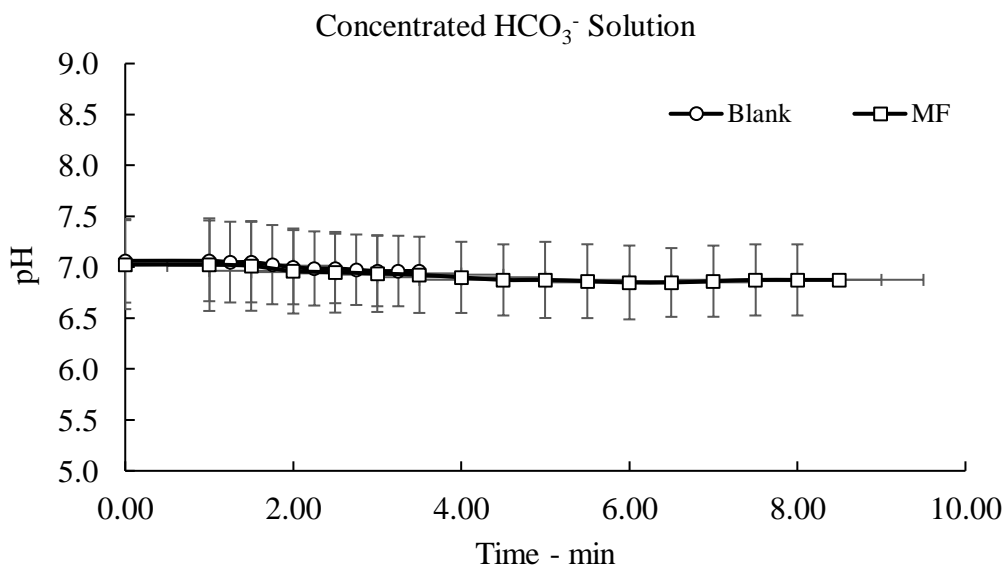


Figure 4-4 - Effect of magnet field exposure upon the pH level of high concentration bicarbonate solution

4.2. Concentrated Ca²⁺ Solution

In a similar manner to the high concentration bicarbonate ion testing, the response of the brine solution containing high concentrations of calcium ions was evaluated by measuring the pressure drop across the capillary tube and the level of electrical conductivity with time. From **Error! Reference source not found.**, the exposure to the magnetic field appears to have the opposite effect upon the formation of scale in comparison to the bicarbonate solution leading to tube blockage faster than the corresponding blank trials. After the application of the magnetic field demonstrated an inhibitory effect upon scale formation of high concentration bicarbonate solution, the opposite effect has been observed for high concentration calcium solution with the magnetic field instead promoting the formation of scale. On average, the time required to completely block the capillary tube under exposure to the magnetic field was 87 minutes. However, the time required to block the same tube under the same conditions but without exposure to the magnetic field was 103 minutes, corresponding to an increase in the scale formation rate of 15.5% on average.

Therefore, it can be concluded that at the high calcium concentration tested within this study, the molecular separation of the ionic species did not occur to the same extent as the concentrated bicarbonate solution, instead promoting the formation of scale. It was theorised that due to a large amount of calcium ions present, an internal clot-like build-up of the calcium ions began to occur within the capillary tube leading to tube blockage. The accumulation scale is illustrated in **Error! Reference source not found.** where due to the poor separation of calcium by the magnetic field, calcium is free to interact with the bicarbonate ions leading to scale formation. As scale formation proceeds, the scale restricts the area of flow through the capillary tube further negating the separation produced by the magnetic field. A lower ratio of calcium to the bicarbonate species may provide a better scale inhibition response more in line with the results generated for test one.

The findings of this study also highlights the different potential responses of mineral ions when exposed to a magnetic field. These responses are dependent on the concentration of ions and most importantly the type of ion whether a bicarbonate, or calcium within the brine solution at the time of magnetic exposure. Although, high bicarbonate findings are supported by the results of Higashitani, Kage, Katamura, Imai and Hatade [29] who observed a similar scale inhibition response of bicarbonate ions under the exposure of a magnetic field but he could not replicate the same results for calcium ions. The findings may help to explain the uncertainty of magnet

treatments in reducing the occurrence of scale formation and clarify the reasons for success or failure of the use of such treatments when applied in industry.

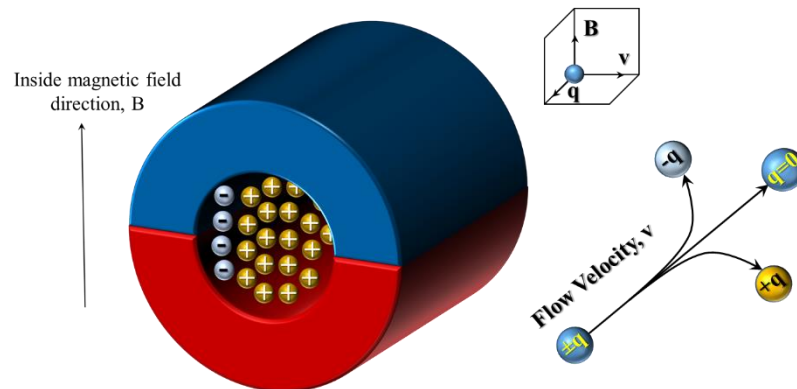


Figure 4-5 Theorised calcium accumulation following magnetic exposure

Furthermore, the electrical conductivity of the high concentration calcium solution to the applied magnetic field demonstrated an opposite response to that of the bicarbonate solution. The application of the magnetic field to the calcium solution instead resulted in increase in electrical conductivity when compared to the blank samples as shown in Figure 4-7. Ayrapetyan, Grigorian, Avanesian and Stamboltsian [56] reported that the increased electrical conductivity was dependent upon the high calcium concentration within the system. However, this does not fully explain the clear difference in electrical conductivity experienced between the exposed and non-exposed solutions. Instead, it may be considered that the application of the magnetic field, in a similar manner to the bicarbonate solution, influenced the structure of the calcium ion leading to a change in electrical conductivity as discussed in Section 4.4.

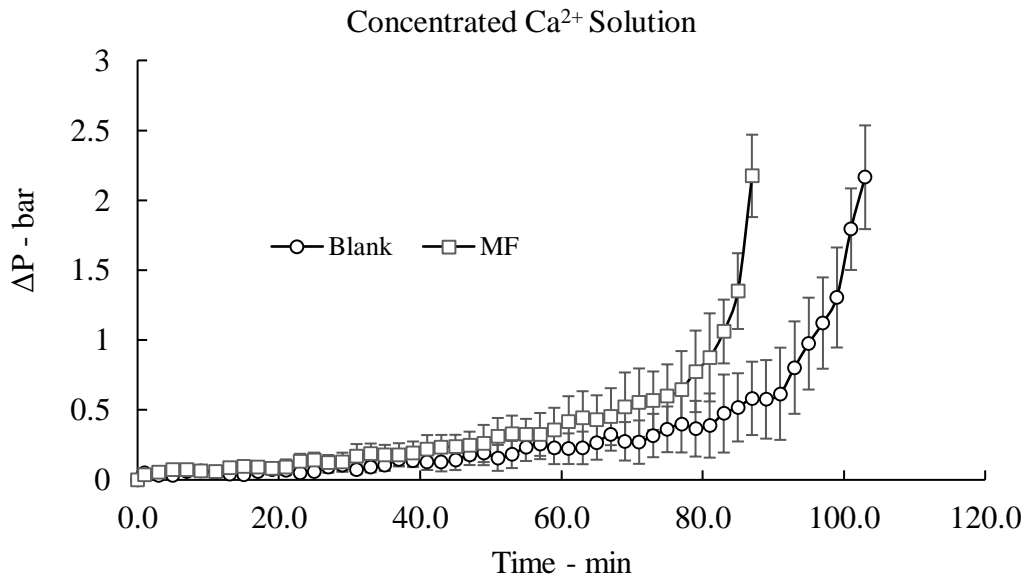


Figure 4-6 Effect of magnet field exposure upon the tendency of high concentration calcium solution to form scale

The reduced hydration layer thickness of the calcium ions under magnet exposure may also play a further role in influencing the scale formation tendency of the high concentration calcium solution. The reduction in hydration layer thickness of the calcium ion when exposed to the magnetic field may facilitate the interaction between the calcium and bicarbonate species resulting in the promoted scale formation experienced within this study for high concentration calcium solutions. In contrast, the increased hydration layer thickness experienced by the bicarbonate ions, indicated by decreased conductivity measurements may have contributed to the inhibition of scale formation.

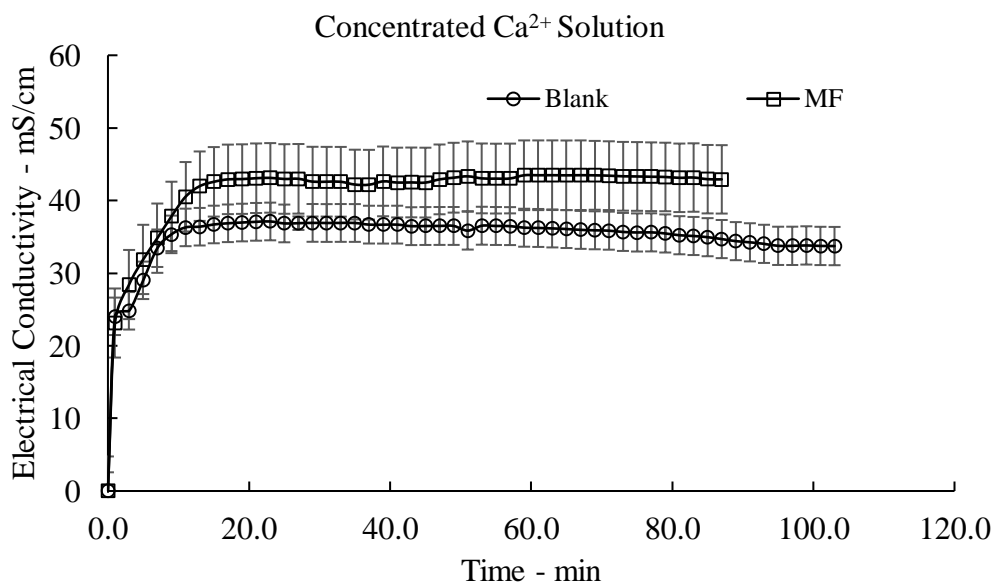


Figure 4-7 - Effect of magnet field exposure upon the electrical conductivity of high concentration calcium solution

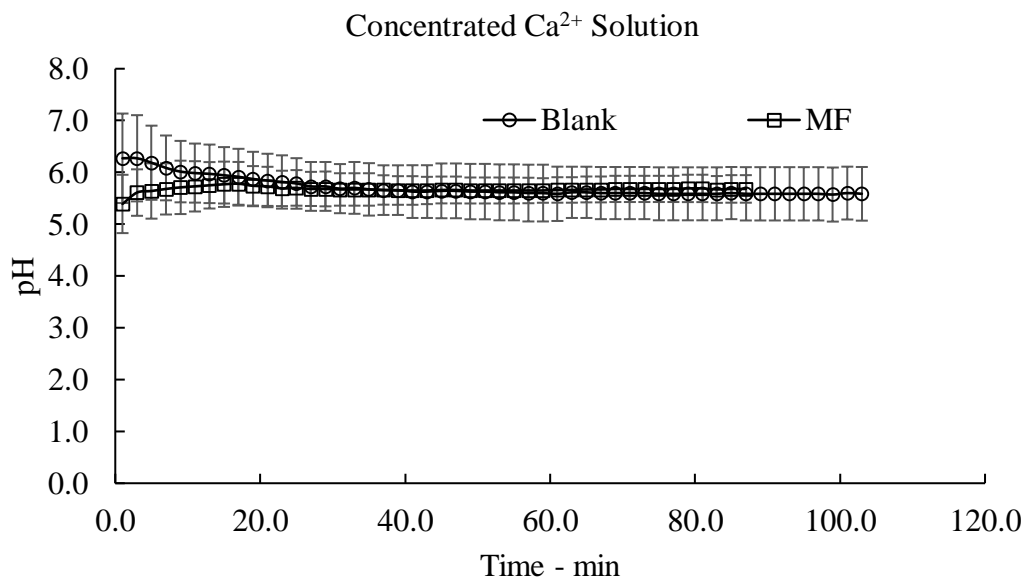


Figure 4-8 - Effect of magnet field exposure upon pH level of high concentration calcium solution

4.3. Equal Concentration of Bicarbonate and Calcium Ions Solution

After observing interesting results whilst using opposing amounts of ionic species, a final test was conducted using a brine solution composed of equal amounts of calcium and bicarbonate. The brine solution used during tested was composed of approximately 700 ppm of the respective ions. The relationship between pressure changes over time is illustrated by Figure 4-9 where a similar trend to that observed for the high concentration bicarbonate solution was produced. However, the equal concentration brine solution required a longer time frame to achieve full blockage of the capillary tube than the high concentration bicarbonate solution. Furthermore, on average, the discrepancy between the time taken to achieve full tube blockage of the exposed and non-exposed tests is greatest for the bicarbonate-rich solution. Thus, it appears that the magnetic effect upon scale formation was greatest for the highly concentrated bicarbonate brine. Overall, it has been established that the exposure to the magnetic field can provide a scale inhibiting effect for brine solutions containing equal amounts of calcium and bicarbonate, or where the solution contains greater amounts of the bicarbonate species.

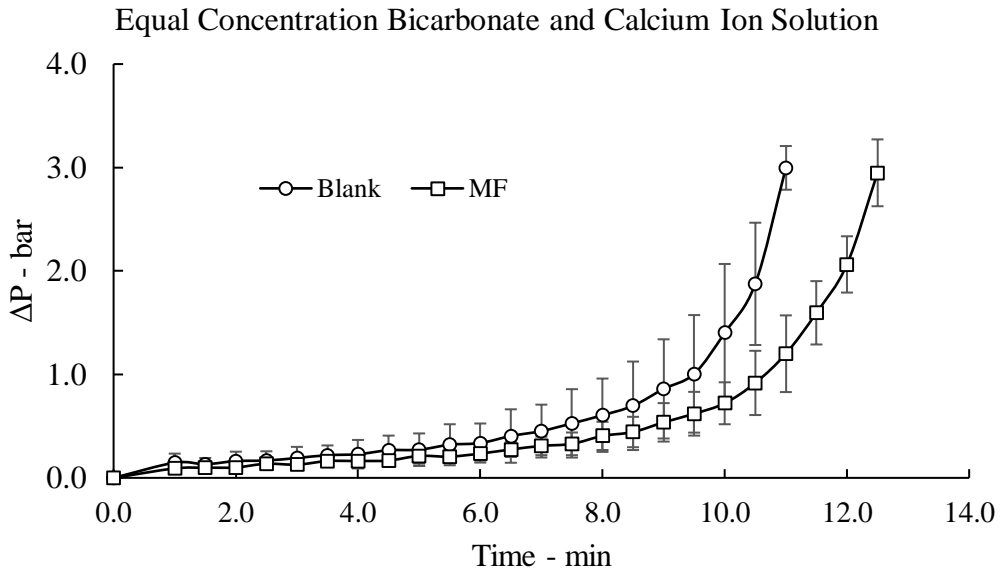
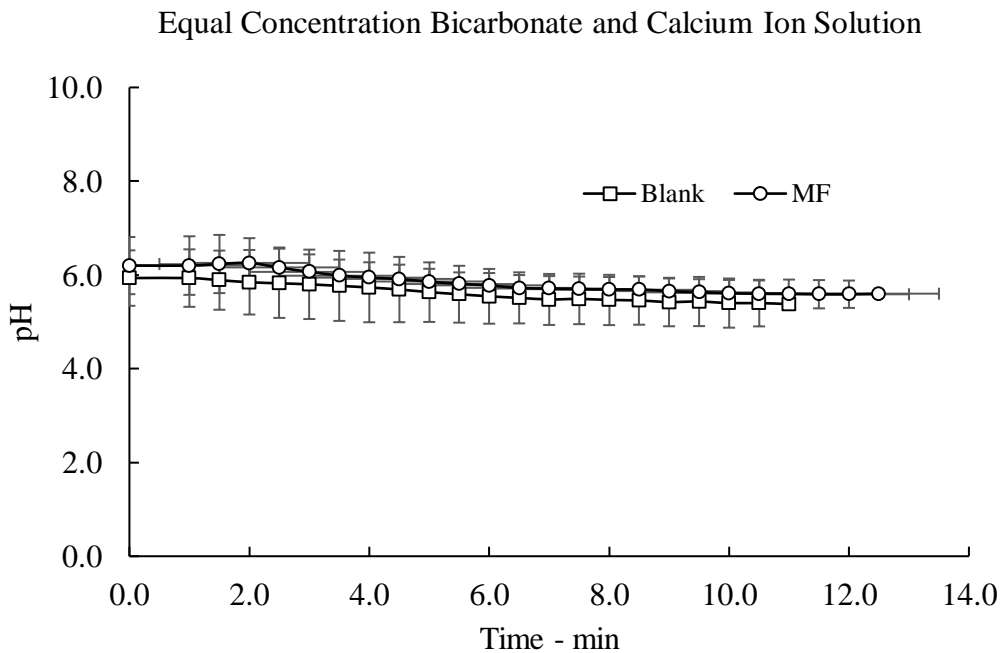


Figure 4-9 - Effect of magnet field exposure upon the tendency of equal concentration solution to form scale

Furthermore, exposure of the equal-concentration ion calcium bicarbonate solution to the magnetic field showed a significant influence upon the electrical conductivity measured. As



shown in , the electrical conductivity readings measured after exposure to the magnetic field were on average noticeably less than the corresponding tests conducted without exposure. This outcome is in line with the previous results generated during the tests conducted with a high concentration of the bicarbonate species, however, to a greater extent.

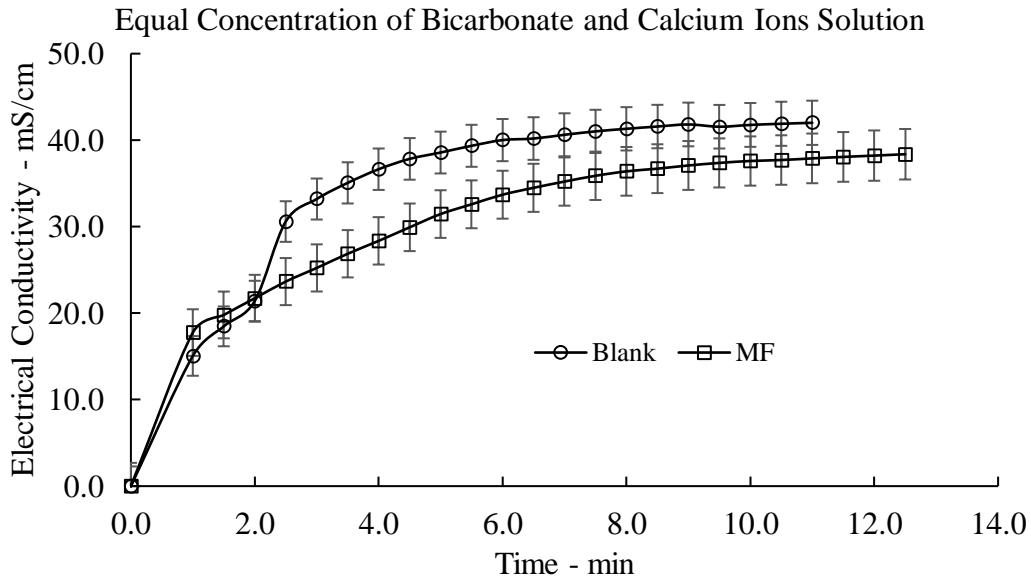


Figure 4-10 Effect of magnet field exposure upon the electrical conductivity of equal concentration solution

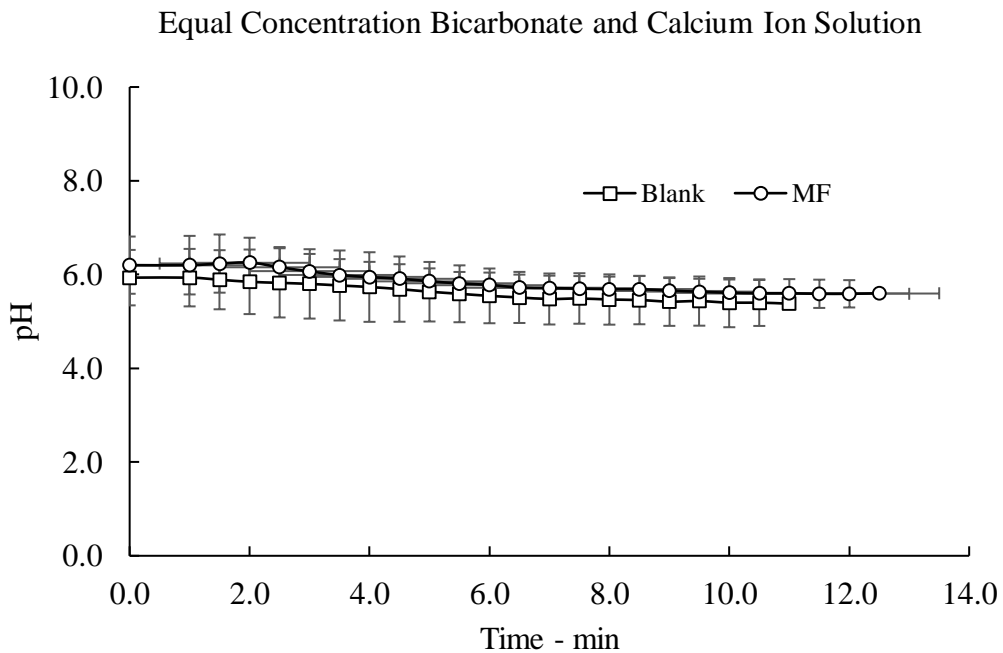


Figure 4-11 Effect of magnet field exposure upon pH level of equal concentration solution

4.4. Magnetic Field Influence upon the Hydration Shell of Ionic Species

It was observed during experimental testing that the solutions containing high concentrations of bicarbonate and calcium generated different responses when evaluated under a magnetic field in terms of electrical conductivity. The difference in response can be attributed to the structure and thickness of the respective ionic species' hydration shell and their response to

magnetic exposure. Through the research conducted by Holysz, Szczes and Chibowski [53], it has been determined that there is an inversely proportional relationship between the hydration shell thickness of the ions and the electrical conductivity of solution. As such, the decrease in electrical conductivity observed for high bicarbonate testing (Figure 4-3) can be attributed to an increase in the hydration shell thickness of the bicarbonate ion due to manipulation by the magnetic field. In contrast, the calcium ions experienced a reduction in hydration shell thickness after magnetic exposure causing an increase in electrical conductivity when compared to the blank test (Figure 4-7) a conclusion in line with the hypothesis of Higashitani, Kage, Katamura, Imai and Hatade [29], Oshitani, Yamada, Miyahara and Higashitani [39] and Holysz, Szczes and Chibowski [53].

In comparison to bicarbonate ions, as per Table 4, calcium ions have a much greater hydration shell thickness, Δr , Table 4. Figure 4-12 illustrates the difference in hydration shell thickness of calcium and bicarbonate ions within solution prior to magnetic exposure and the relationship between hydration shell thickness and electrical conductivity. Whilst

Figure 4-13 illustrates the effect of magnetic exposure upon the hydration shell thickness of the calcium and bicarbonate ions. The hydration shell represents the accumulation of water molecules within the “ionic atmosphere” of an ion due to the attraction of either the positive and negatively charged poles of the polar water molecule to the ionic. Marcus [54] and Holysz, Szczes and Chibowski [53] reported that the smaller the ion, the greater the amount of water molecules that will interact around the ion species (Figure 4-14). Therefore, a small ion has a greater tendency to polarize the surrounding water molecules and will hence have a greater hydration shell radius in comparison to larger ions [57-59].

Table 4 - Radius of ions, r , the thickness of ion hydration shell, Δr , and the number of water molecules in the shell, n [53, 54, 60]

Ions	r, nm	$\Delta r, nm$	n	Ionic mobilities in water
				<i>at 25°C, $u/m^2s^{-1}V^{-1}$</i>
H ⁺	0.030	0.300	12.0	36.30*10 ⁻⁸
Mg ²⁺	0.072	0.227	10.0	5.50*10 ⁻⁸
Ca ²⁺	0.100	0.171	7.2	6.12*10 ⁻⁸
Na ⁺	0.102	0.116	3.5	5.19*10 ⁻⁸
OH ⁻	0.133	0.079	2.7	20.50*10 ⁻⁸
HCO ₃ ⁻	0.156	0.059	2.3	4.61*10 ⁻⁸

Ions	r, nm	$\Delta r, nm$	n	Ionic mobilities in water
				at 25°C, $u/m^2s^{-1}V^{-1}$
CO_3^-	0.178	0.076	4.0	$7.18 \cdot 10^{-8}$
Cl^-	0.181	0.043	2.0	$7.91 \cdot 10^{-8}$

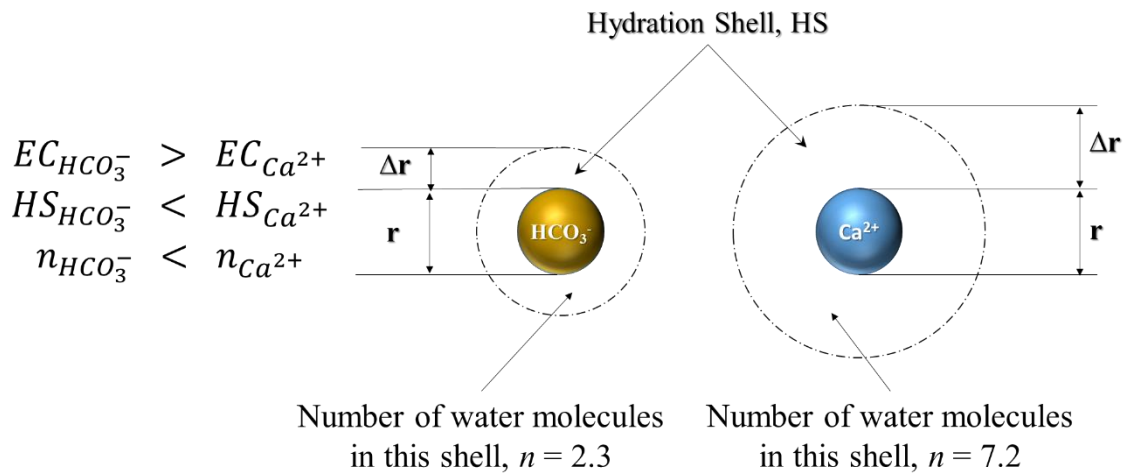


Figure 4-12 - The relationship between hydration shell and electrical conductivity with respect to number of water molecules [53, 59, 60]

The inverse relationship between hydration shell thickness of the ionic species and the electrical conductivity of the solution occurs due to the accumulation of the water molecules around the ions. As the hydration shell thickness increases, the accumulation of water molecules effectively acts as an insulating barrier reducing the overall effective charge of the ion and hence a reduction in electrical conductivity, refer to Table 4. This relationship is illustrated within

Figure 4-13 for the bicarbonate ion in a similar manner to that experienced within the high concentrated bicarbonate testing given by Figure 4-3. In contrast, the thickness of the calcium ion after magnetic exposure was theorized to have been reduced leading to the increased electrical conductivity measurements observed in Figure 4-7. Furthermore, as the hydration shell thickness grows, the ion will tend to react more slowly with surrounding ions due to the insulating effect of the water molecules [57-59, 61]. Therefore, the ability of the ionic species to interact with the opposing ion to form scale is inhibited an outcome in line with the high bicarbonate solution testing where scaling was inhibited.

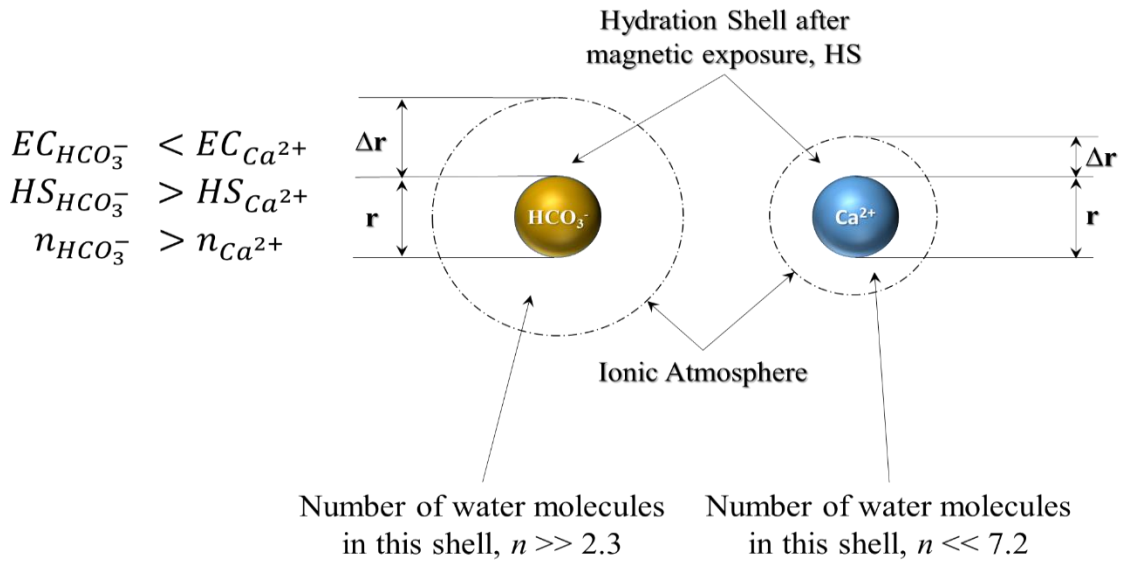


Figure 4-13 - Hydration shell of calcium and bicarbonate ions after diametrically magnetic field exposure [53, 59, 60]

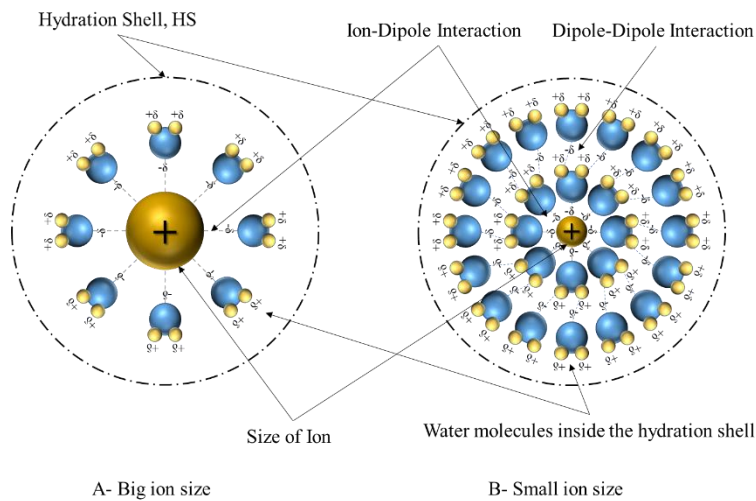


Figure 4-14 - Comparison of hydration shells of large and small ions

The primary reason for the increase in hydration shell thickness around the bicarbonate ions is the rearrangement of water molecules (polar molecules) after magnetic field exposure. As discussed previously, polar molecules such as water are influenced by the application of a magnetic field causing them to adopt a more orderly arrangement, refer to Figure 2. This rearrangement leads to a more organized pattern of water molecules hence allowing a greater number of water molecules to fit within the hydration shell of the ion. However, it was observed experimentally that the opposite effect occurred when evaluating the effect of magnetic exposure upon high calcium concentration solution with respect to the calcium ion. Instead, the magnetic field lead to a reduction in the hydration shell thickness of the calcium ion as

evident through increased electrical conductivity measurements and tendency to form scale compared to blank tests. Overall, different responses of the cations and anions tested within this study to magnetic field exposure was observed in terms of effect upon scaling and electrical conductivity.

5.0 Conclusion

Within this study, the application of magnetic field treatment has been performed to evaluate its influence upon the scale formation tendency of sodium bicarbonate solutions of varying concentrations. The extent of scale formation was evaluated using a Dynamic Scale Loop system by measuring the increase in pressure across a capillary tube as the formation of scale proceeded. In contrast to similar studies performed to evaluate the effects of magnetic exposure upon the behaviour of ionic species, an appreciable impact upon particle behaviour in the form of inhibited scale formation and electrical conductivity was achieved using only brief magnetic exposure. Many studies use long term exposure to magnetic fields to evaluate their impact, however, the results of this study have conclusively demonstrated that only brief exposure (2.5 seconds) to a strong diametric magnetic field can significantly influence particle behaviour. Furthermore, prior studies performed to evaluate magnetic treatment tend to use singular or multiple rectangular magnetics arranged around the fluid flow using either Class 1 or 4 magnetic arrangement as shown in Figure 1-1. In comparison, the results of this study were generated using a Class 4-A magnetic arrangement utilising a circular ringed shape with fluid flow occurring through the centre of the magnet (**Error! Reference source not found.**) making the results of this study unique.

Through the results generated using the DSL system, three conclusions were drawn regarding the use of magnetic field treatment to inhibit the scale formation of calcium carbonate in water systems. Firstly, the extent of scale formation, whether inhibited or promoted, is dependent upon the ratio of bicarbonate to calcium. Through the tests conducted, it is apparent that the amount of bicarbonate present plays a key role in making the application of magnet treatment for preventing scale formation applicable to the brine solutions tested. Of the tests conducted, where bicarbonate was of greater or equal concentration to the calcium ions, appreciable inhibition of scale formation was achieved suggesting the bicarbonate are more responsive to the effects of the applied magnetic field compared to the cations. The inhibition of scale formation was attributed to the intermolecular separation of the calcium and bicarbonate ionic species generated by the Lorentz force as the solution flowed through the magnetic field.

Following exposure to the magnetic field, the separated ions within the solution had sufficient magnetic memory to ensure the formation of scale was inhibited. However, due to the large amounts of calcium ions present during the high calcium concentration testing, the same behavior could not be repeated due to a theorized clot-like build upon within the capillary tube that lead to interaction between the calcium and bicarbonate forming scale deposition. Furthermore, it should be noted that the separation of charged particles achieved through magnetic exposure can only be maintained during laminar flow. Turbulent flow of the solution would promote mixing of the separated charged particles effectively nullifying the effects of magnetic exposure.

Secondly, the exposure of the brine solutions to the applied magnetic field had a significant impact upon the electrical conductivities measured. A considerable reduction in electrical conductivity of the high concentration bicarbonate and equal concentration solutions was observed during testing and was attributed to the influence of the magnetic field on the structure of the ionic species. The results of the tests conducted were in line with previous testing performed by various authors who concluded that the hydration shell thickness of the bicarbonate and calcium ions are subject to manipulation by magnetic fields leading to changes in electrical conductivity. Furthermore, it was observed that the electrical conductivity measured at the outlet of the DSL system steadily increased as scale formation proceeded. It was therefore concluded that the measurement of electrical conductivity may provide an indirect measure of the extent of scale formation with a pipeline.

Finally, due to the successful inhibition of scale formation through the influence of the magnetic field treatment applied during experimental testing, it can be suggested that magnetic field treatment may provide an eco-friendly scale inhibition strategy in place of traditional chemical scale inhibitors. Furthermore, magnetic field treatment for scale inhibition may provide a more cost effective method to prevent the formation of scale due to the one-time cost of a magnetic treatment system being outweighed by the continued cost of chemical scale inhibitor application with time. However, the applicability of magnetic field treatment on large scale pipelines is yet to be fully evaluated.

6.0 References

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