



**University of  
Durban-Westville**

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School of Engineering  
Department of Chemical Engineering

**The Study of the Mechanism of  
Magnetic Water Treatment  
for the Prevention of  
Scale and Corrosion**

*MSc. Thesis*

by

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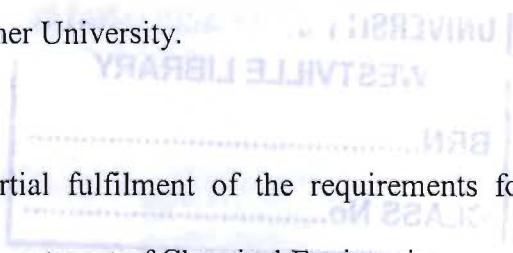
# DECLARATION

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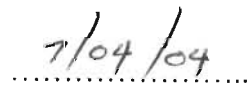
I, Sudesh Rathilal, student no.: 9038743, hereby declare that this thesis is the result of my own investigation and research and that it has not been submitted in part or in full for any other degree or to any other University.

This thesis is submitted in partial fulfilment of the requirements for Masters of Science in Engineering in the Department of Chemical Engineering.



  
.....

S Rathilal

  
.....

Date

This thesis is dedicated to my daughter, Simran.  
Without you by my side, this would not be possible.

## **ACKNOWLEDGMENTS**

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## ABSTRACT

Scaling and corrosion cost industries all over the world millions of rands each year. Chemical treatment of water to prevent scale is expensive and can be hazardous. As a result industry is always looking for new, cheaper alternate methods of reducing scale. One such method is magnetic water treatment. Magnetic water treatment involves passing hard water (the main cause of scale) through a magnetic field. This method favors the precipitation of calcium carbonate in the form of aragonite instead of calcite. Aragonite is a softer, less tenacious material that does not adhere to the walls of pipes or heating surfaces. These particles remain in suspension and may settle out somewhere along the system where the velocity of the water has been reduced.

A simple bench-top heating system was set up to determine whether magnetic treatment works and, if it does, to determine the optimum conditions under which it operates. A saturated solution of calcium carbonate was circulated through the heating system with, and without the magnets, so that comparisons could be made.

The precipitate was analysed (via X-ray diffraction) to calculate the proportions of calcite and aragonite, while atomic absorption was used to test the hardness of the filtrate. This gave an indication of the effectiveness of the magnetic system. pH graphs and absorption graphs were plotted to compare the rates of precipitation. The precipitate was also observed under the electron microscope in order to view the different structures of calcite and aragonite.

Experiments were carried out at different temperatures and different flow rates in order to test the effect of these parameters on the magnetic system.

Results showed that the magnetic field increased the rate of precipitation and caused aragonite rather than calcite to be formed. This was in contradiction with most literature surveyed, which stated that magnetism increased the dissolution of calcium carbonate. Results indicated that the higher the temperature, the greater was the rate of precipitation and as a result, the greater the amount of aragonite formed, even without the magnets. Increased flow rate also increased the amount of aragonite formed. As a result hereof, conclusive results could not be obtained at high temperatures and high flow rates.

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## **CHAPTER 1**

### **INTRODUCTION**

The problems caused by scale formation and corrosion costs industries all over the world millions of rands each year. The build-up of scale is estimated to cost the UK industry over £800 million each year.

Scaling may be caused by the use of hard waters in a system. The water may be hard as it comes in with the feed to the system or it may become hard as a result of recycling. If hard water is used in a domestic system, lime may build up in and on the plumbing network. This will result in a decrease in the efficiency of the domestic water system due to increased energy consumption. Similar problems are encountered when hard water is used in a commercial system. These problems are, however, elevated. Under industrial use of hard water, the system will experience reduced efficiency, a shorter life period as well as an increase in the energy consumption.

If hard water is used in a heat exchange system some of the dissolved minerals may precipitate from the water resulting in scale formation on the heat exchange surfaces. This results from pressure and temperature changes in the heat exchange system. The scale acts as an insulation that results in a reduction in the heat transfer efficiency as well as a restriction of water flow through the system.

The traditional water softening which involves the addition of various chemicals in order to change the behavior of the dissolved minerals and thus eliminate the problems caused by scale and corrosion has numerous drawbacks. These include high costs and continuing expenses, safety hazards in chemical handling, pollution of treated water, etc. In some cases the chemical treatment is not feasible, for example when large volumes of water are to be treated. As a result lines and equipment that become scaled have to be disassembled and either mechanically or chemically cleaned which results in escalating time and labor costs.

Due to the unfeasibility of traditional water treatment many years of research have gone into finding alternate methods of scale and corrosion prevention. This thesis seeks to add to the research carried out on the method of magnetic treatment of water to prevent scale and corrosion.

The subject of alternate methods of scale reduction and suppression is controversial. The debate is understandable due to the fact that many years of positive effects from industrial applications have been undermined by the apparent lack of good results from laboratory tests. Large chemical companies also stand to lose millions of rands if alternate methods of scale reduction are implemented on a large scale.

Magnetic treatment was first practically applied by Theo Vermeiren in 1945 [10] for decreasing the formation of scale in steam boilers. Since then the application of magnetic units in industry has increased drastically and is continuing to increase. Some of the advantages of the magnetic treatment are that it is non-chemical, non-polluting, and easily installed. It may be attached to the outside of the line so that it is not necessary to cut the lines being treated in order to install the magnetic unit.

The main objectives of this thesis are: (1) to determine whether the magnetic field affects the water and its constituents in any way (so as to determine whether magnetic treatment works or not); (2) to find the optimum conditions under which the system works; and (3) to formulate a theory behind the mechanism by which the magnetic field, generated by the magnetic unit, affects the fluid passing through it and thus prevents scale and corrosion.

## CHAPTER 2

### LITERATURE REVIEW

Magnetic water treatment is a fairly new technology in South Africa and not much literature was available locally. A search was also done with the British Library and Document Support Centre; however, most of the literature found were on successful applications of the treatment and had very little to do with the theory behind the actual working of the system.

#### 2.1 Causes of Scale and Corrosion

The problems associated with the build-up of scale costs industry all over the world millions of rands every year. In 1990 scale build-up was estimated to cost the British industry over £800 million annually, whereas in 1992 this had escalated to over £850 million annually. It is now estimated to cost over £1 billion per year. Such costs can be attributed to cleaning, increased pumping costs, or the reduced thermal conductivity of scaled surfaces (heat transfer is decreased by 95% by a calcium carbonate scale layer 25 mm thick) [25,51,52].

The most common deposits of scale are calcium carbonate, phosphate and sulphate, barium sulphate, magnesium hydroxide, zinc phosphate and hydroxides and silicates of iron and all mineral salts present in water used extensively in a majority of process applications. However calcium carbonate is by far the main constituent of scale.

If hard water is used in a heat exchanger, it is subjected to temperature and possibly pressure changes. As a result some of the dissolved minerals may precipitate out of the water and form scale on the heat exchange surfaces and act as insulation thereby reducing the efficiency of the heat transfer and restricting water flow.

Dawson [7] attempted to discuss the chemistry involved in scale formation and described natural waters as “ionic soups.” Due to changes in local conditions the ionic species either combine together to form crystals, or break up into free ions in order to remain in a thermodynamic equilibrium with their environment. He used calcium carbonate (the principle scaling salt found in hard waters) as an example to describe the chemistry of scaling. The equilibrium equation for calcium carbonate is given by equation 2.1.



This equation is true only if calcium carbonate is in an isolated system. Dawson only considered this simple equation in his explanation. However, in water there are numerous other ions that will affect this equilibrium. These ions may react with the calcium and carbonate ions, and thus the equilibrium equation is not as simple as that shown in equation 2.1. However, calcium carbonate is the main constituent of scale, and therefore if this can be reduced so will the scaling.

There are basically two factors that affect scale formation from fluids: solubility and nucleation. Scale formation occurs as a result of the deposition of a precipitate from a saturated or supersaturated solution. The main causes of supersaturation in liquids



include concentration of the solution, temperature and pressure changes and changes in pH. Changes in the above result in changes in the solubility of the scale forming compounds. Low solubility is one of the major effects in scale formation. Nucleation is the other effect that eventually has to occur in order to cause the precipitate to grow [54].

Since supersaturation is a prerequisite for precipitation, Dawson defined 'Supersaturation ratio' as follows in order to determine whether a water can scale:

$$Sr = \frac{[Ca^{2+}]_a [CO_3^{2-}]_a}{[Ca^{2+}]_{eqm} [CO_3^{2-}]_{eqm}} \quad [2.2]$$

where, square brackets refer to the ion concentrations (mole/litre) of the free calcium and free carbonate;  
 'a' refers to the actual concentrations; and  
 'eqm' refers to the equilibrium concentrations.

If  $Sr > 1$  scaling can occur; if  $Sr < 1$  then scaling cannot occur, but dissolution can. If  $Sr = 1$  then the system is saturated and, providing there are no changes in the physical properties of the system, neither precipitation nor dissolution would take place. Therefore scaling is controlled by the equilibrium and free ion concentrations of  $Ca^{2+}$  and  $CO_3^{2-}$  ions in any water [7].

Dawson [7] described the 'overall carbonate equilibrium path' available in hard water, and explained how temperature and pH changes affected these reactions. The reactions are shown in Fig. 2.1 below.

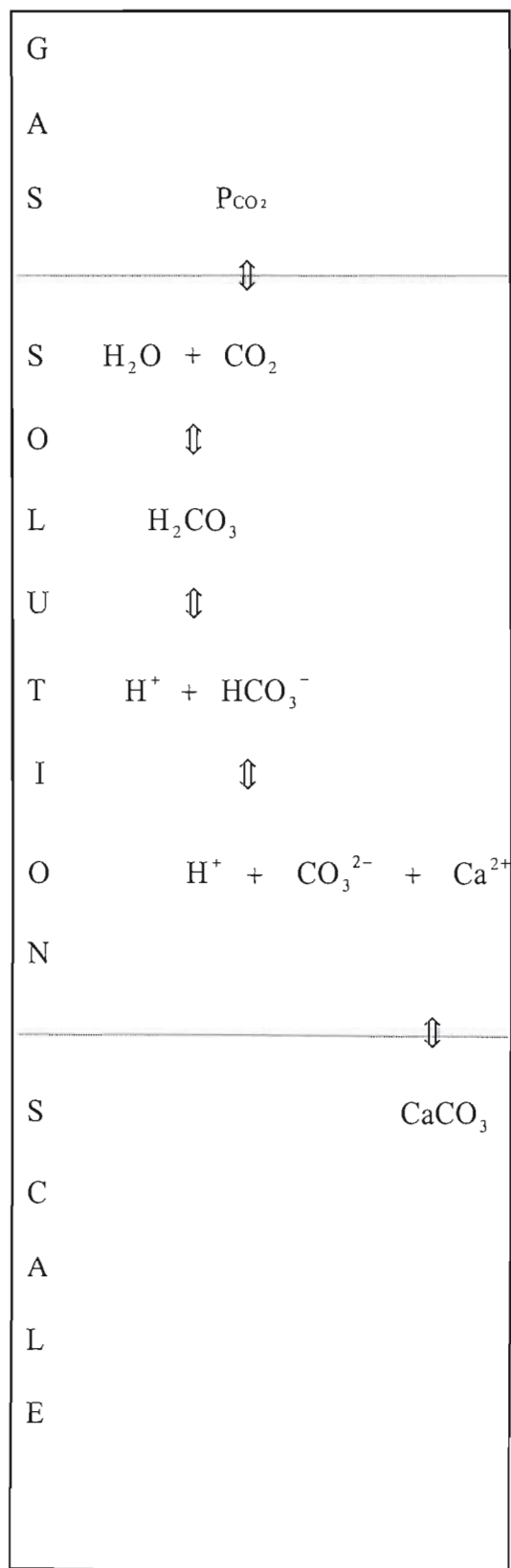


Fig. 2.1 – Carbonate Equilibrium Chain in Hard Water [7]

If the temperature increases (e.g. in a boiler) the bicarbonate ion thermally decomposes to form carbonate ions. As a result the supersaturation ratio is increased, thereby increasing the possibility of scale formation. If the pH increases, the water will tend to produce more  $H^+$  ions to maintain the  $H^+/OH^- \Leftrightarrow H_2O$  equilibrium. It does this by decomposing carbonic acid, thereby producing  $CO_3^{2-}$  ions and increasing the supersaturation ratio.

The supersaturation ratio  $Sr$  is affected more by an increase in pH than an increase in temperature. A simple example is that a temperature increase of  $80^\circ C$  takes a water that is close to saturation at  $10^\circ C$  to a supersaturation ratio of between 3 and 4. However, a change in pH from 7.0 to 8.0 (one pH unit) increases  $Sr$  to around 15. Scaling is now five times as rapid (or five times as likely to occur) than under the temperature increase shown above.

In a pipeline, scale is formed on the inside due to deposition of insoluble salts (mainly  $Ca^{2+}$  and  $Mg^{2+}$ ). This scale formation eventually leads to internal corrosion. Initially fine pits appear inside the pipe, then spotted corrosion starts and finally the pipe corrodes uniformly from the inside. In the case of water heaters and other boiler systems, the concentration of insoluble salts increases and  $CO_2$  gas is released from the  $CaCO_3$  solution with a rise in temperature, which also increases the pH value of the water.

Fluid-Tech International Corporation [10] provides a table (Table 2.1) of average values of thermal efficiency loss of boilers, water heaters, heat exchangers, etc. with various thicknesses of scale and shows the importance of scale free conditions.

Thickness of Scale (mm)	Loss of Thermal Efficiency	Coal Wasted per Ton of Coal Used (kg)	Oil Wasted per 1000 litres of Oil Used (litres)	Gas Wasted per 1000 m <sup>3</sup> of Gas Used (m <sup>3</sup> )
0.40	4%	36	40	40
0.79	7%	63	70	70
1.59	11%	100	110	110
3.18	18%	163	180	180
4.76	27%	245	270	270
6.35	38%	345	380	380
9.53	48%	435	480	480
12.70	60%	544	600	600
15.88	74%	671	740	740
19.05	90%	816	900	900

**Table 2.1 – Thermal Efficiency Loss Due to Scale [10]**

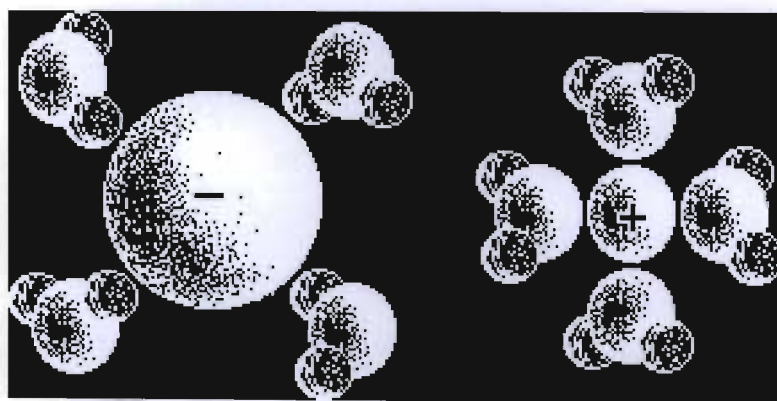
The amount of energy used in heating and cooling applications increases with the thickness of the scale on the heat exchange surface due to the low thermal conductivity of the scale. Table 2.2 [33] shows an estimate of the increases in energy consumption as a function of scale thickness for a simple heat exchanger.

Scale Thickness (mm)	Increased Energy Consumption (%)
0.8	8.5
1.6	12.4
3.2	25
6.4	40

**Table 2.2 – Energy Consumption versus Scale Thickness [33]**

Water Chemistry

When calcium carbonate dissolves in the water, the dipolar water molecules surround the individual  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions and form a hydration shell (Fig 2.2). The strongly bound layer close to the surface of the ion is called the Stern Layer. Those molecules further away from the core ion make up a diffuse layer, more loosely bound to the ion. The chemistry and physics of these hydration shells keep the positively charged and negatively charged ions separated and in solution. Since the  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions are kept far apart, they cannot recombine to form calcium carbonate. Any disturbance of these protective shells allows the positive and negative ions to approach (attract) and possibly attach forming a floc.



**Fig. 2.2 – Hydration Shells Forming on Dissolved Ions**

Within the diffuse layer is a notional boundary, inside which the ion and its associated water molecules (Stern Layer) act as a single entity, diffusing through the dispersion together. The plane at this boundary is known as the surface of hydrodynamic shear, or the slipping plane, and its potential, the Zeta potential (a measure of the magnitude of repulsion or attraction between particles). When considering the relative behaviour

of two particles of unlike charge, their potential interaction in polar waters is not governed by the electrical potential at the surface of the particle, but rather by the potential that exists at the slipping plane [19].

## 2.2 Traditional Water Treatment Methods

The traditional methods of water treatment in industry are either by chemical additions or ion exchange. Common commercial types of hard water treatment systems include chemical water softeners, water filters and packed-bed water softeners.

Chemical water softeners are chemicals that control water hardness. There are basically two types, precipitating and non-precipitating. Precipitating water softeners include washing soda and borax that form an insoluble precipitate with calcium and magnesium ions, thus reducing the hardness of the water. The precipitate makes the water cloudy and, if not removed, can build up on surfaces. The alkalinity of the water is increased and can damage many materials, including skin. Non-precipitating softeners use complex phosphates to sequester calcium and magnesium ions. There is no precipitate to form deposits and alkalinity is not increased.

Water filters generally come in two forms, portable ion exchange and reverse osmosis. Both are used to filter out harmful or unwanted particles before the water is used for human consumption. Reverse osmosis works by forcing water through a semi-permeable membrane that stops certain particles from passing through. Portable water filters uses a cartridge containing activated carbon and ion exchange resin. The carbon adsorbs and helps reduce levels of chlorine and chlorine compounds, as well as

pesticides, colour and other organic substances to improve taste and appearance. The ion exchange resin works to reduce temporary hardness.

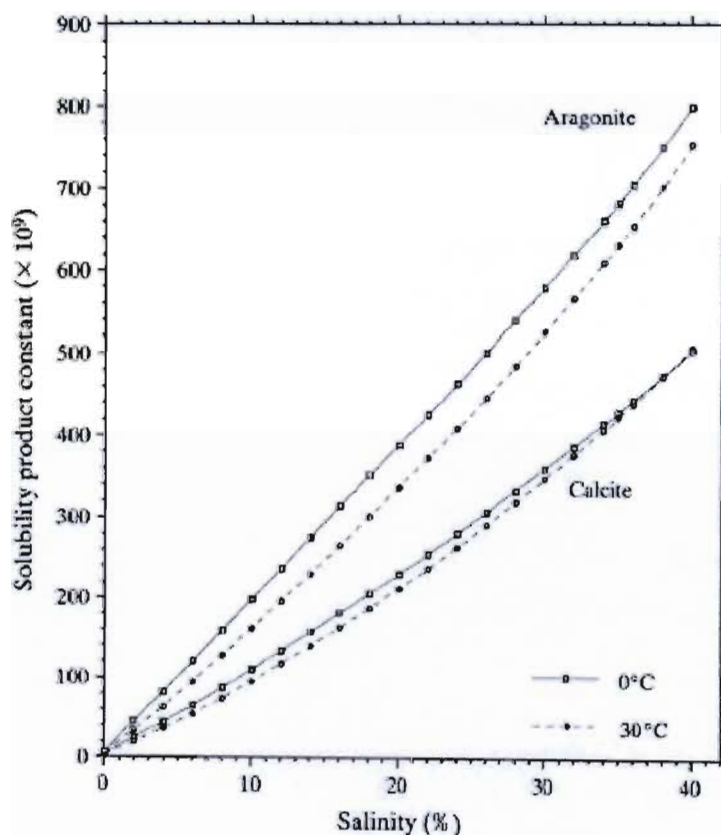
Packed bed water softeners also operate on the ion exchange process. Water passes through a media bed (usually sulfonated polystyrene beads) supersaturated with sodium. The elements responsible for hardness attach themselves to the resin beads while sodium is released simultaneously into the water. When the resin becomes saturated with calcium and magnesium, it is recharged by passing a brine (NaCl) solution through it. The sodium ions replace the calcium and magnesium ions, which are discharged in the waste water [27]. One of the disadvantages of the ion-exchange treatment is that regeneration of the crystals may require expensive chemicals. Even modern ion-exchange plants that operate automatically require expensive electronics.

Chemicals may be used to combat scale formation in most cases, however these chemicals are a threat to the environment and are not always the most suitable or cheapest method of preventing scale. Typical chemicals used for the chemical treatment are mixtures of sodium hydroxide and sodium aluminate, complex chelate compounds, etc. However, the main disadvantages of the chemical treatment are that the water needs to be analysed chemically and chemical dosing must be accurate [8].

Other drawbacks of the chemical treatment are high costs and continuing expenses, safety hazards in chemical handling, pollution of treated water, etc. Chemical treatment is also not feasible if large volumes of water are to be treated. Where chemical treatment is not practical, lines and equipment that become scaled must

usually be disassembled and either mechanically or chemically cleaned, which involves a great expense of time and labour.

The addition of a sodium salt increases the solubility of calcium carbonate and thus prevents/reduces the precipitation that forms scale. Fig. 2.3 [15] shows the effect of the solubility on the addition of sodium chloride. It must be noted that aragonite is much more soluble than calcite. This means that if magnetic water treatment can change calcite to aragonite, the addition of a sodium salt will increase the solubility of the calcium carbonate (aragonite).



*The stoichiometric solubility product constants ( $K_{sp} = [Ca^{2+}][CO_3^{2-}]$ ) for calcite and for aragonite in relation to the salinity of the water and at temperatures of 0°C and 30°C.*

**Fig. 2.3 – Effect of Salinity on Solubility of  $CaCO_3$  [15]**



The amount of sodium that must be added to water depends on the initial hardness, as shown by the following table.

<b>INITIAL HARDNESS (ppm)</b>	<b>SODIUM ADDED BY SOFTENING (mg/liter)</b>
17	7.9
86	39.6
171	79.3
342	158.5
685	317.0

**Table 2.3 – Amount of Sodium Added as a Result of Hardness [10]**

### **2.3 Magnetic Treatment**

Magnetic descaling is referred to as the cleaner, greener option, because of the growing pressure from environmentalists against chemical treatment.

The advantage of the magnetic treatment is that no chemicals, or chemical analysis of the water, are required. Permanent magnets (if used) never age and have a virtually unlimited life. The labour requirement is also reduced.

Magnetic treatment is non-polluting, easily installed and virtually maintenance-free. Furthermore, certain magnetic units operate with permanent magnets so that no input

power is required. The magnetic units may be installed to the outside of the lines making it unnecessary to cut the lines being treated in order to install the unit.

Using a magnetic unit to treat hard water (in a cooling tower for example) results in smaller crystals forming throughout the volume of the water rather than a regular crystalline structure that continues to grow over a period of time. The small crystals do not adhere to the heat exchange surfaces, but are carried on through the system and returned to the cooling tower where they settle out as a sludge in the bottom of the tower. The constant water velocity through the system keeps the crystals suspended. The small crystals settle out in the sump of the cooling tower because of the reduced rate of flow. Moreover, scale originally present is likewise removed and transported to the cooling tower.

The sludge in the cooling tower must be removed periodically or it will be carried back through the system. With increasing amounts of the sediment, the water flow may not be sufficient to keep all the solid material in suspension, leading to the sediment being deposited in other areas in the system and causing an increase in head pressures with reduced operating efficiency of the system [10].

The magnetic field has many effects on the scale materials including changes in particle size, crystallinity, crystal morphology, crystal phase, solubility and the rate of precipitation. Since magnetic treatment attempts to change the behaviour of the problem-causing minerals rather than changing the chemical make-up of the water, a chemical analysis of the water before and after the magnetic treatment shows no difference [51].

The actual mechanism by which the magnetic units operate is unknown. At this point in time there are only theories and years of accumulated evidence documenting the effectiveness of this type of treatment.

Donaldson [51] suggested that the effect of the magnetic treatment is based on nucleation sites with charged surfaces that are present in the fluid. The nucleation sites provide the scale-formers with a site to grow on. The charges on the surfaces of the nucleation sites are altered as they pass through the magnetic field. Thus changes occur in crystal size, morphology and solubility. For calcium carbonate, the morphology is changed in such a way so as to precipitate aragonite instead of calcite. The aragonite polymorph of calcium carbonate is a softer crystal and does not adhere to heating and piping surfaces.

The increase in size of the precipitated crystals prevents them from agglomerating in the process fluid thereby reducing the possibility of scale. When the magnetic unit is fitted any hard scale already present is turned into a 'soft gunge' that sticks loosely to the pipes and can easily be removed. If the device is fitted into a clear system (non-scaled system), scale is avoided altogether [51].

It must be stressed again that magnetic treatment does not involve any chemical change in the water. Most water softener manufacturers claim that they make the water soft by taking out the minerals. However, by simply comparing the feel of distilled water, which contains no minerals, to that of artificially softened water proves that this is not true. Water softeners soften water by the method of ion exchange. Hardness-causing calcium and magnesium ions are exchanged for sodium

ions. Therefore instead of calcium carbonate being formed, sodium carbonate is formed (which is an ingredient in common detergents) and this is why the softened water has a slippery feel to it [10].

Water-softener salespersons often say that the softener does not add salt to the water, which is only true in the sense that it does not add sodium chloride (table salt). But sodium, which is the problem-causing element in salt (health hazard to people with heart or blood pressure problems), is added.

Magnetic treatment accelerates the coagulation of suspended matter, the wetting of solid surfaces by water, the adsorption of surface-active substances, and the processes of crystallisation and dissolution. It improves the removal of suspended matter from water, enhances ore-enrichment processes and increases the plasticity of concrete mixture and the strength of concrete, brick and other articles made from binders [12].

The temporary change in the structure of the water caused by magnetic treatment can be observed in the study of the infrared spectrum. The absorption rate increases by 30-40% and then, within a day, returns spontaneously to the normal value. This does not confirm any change in the structure of the water, but shows that some sort of change does occur [40].

Glushchenko and Grishaenko [11] stated that magnetic treatment affects the  $\text{CO}_2$  equilibrium. They used the equilibrium factor for  $\text{CO}_2$  (defined as the ratio of free  $\text{CO}_2$  to combined carbonic acid) as a check to test whether the magnetic treatment was effective or not.

$$K_e = \frac{CO_{2\_free}}{CO_{2\_combined}} \quad [2.3]$$

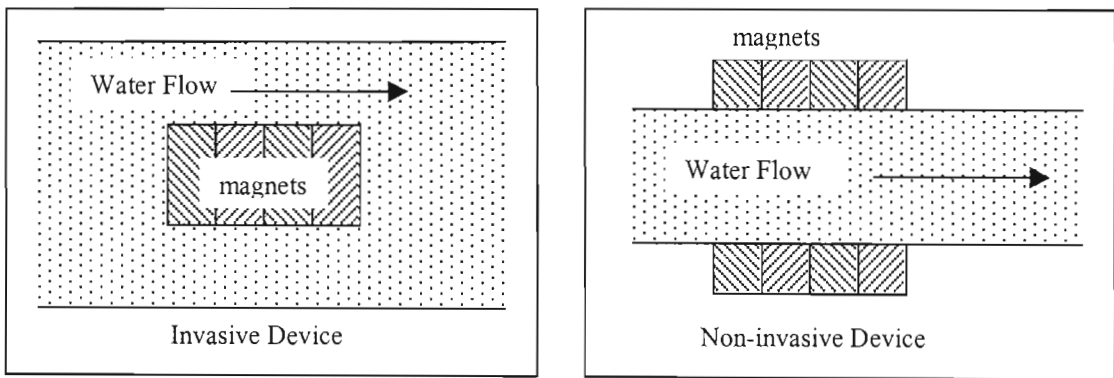
where,  $K_e$  = CO<sub>2</sub> equilibrium factor

This ratio is at constant temperature, thus there must be a certain amount of free carbon dioxide to be in equilibrium with the combined carbonic acid. When  $K_e < 1$ , the magnetisation is effective. The free CO<sub>2</sub> is less than the combined. Therefore, in order to reach equilibrium, the amount of carbonic acid in the solution must be reduced to produce more free-CO<sub>2</sub>. Reducing the amount of carbonic acid reduces the chance of the carbonate ion combining with calcium and magnesium ions to form scale. If  $K_e > 1$  it leads to adverse results. To reach equilibrium, the excess free CO<sub>2</sub> will be combined to form carbonic acid increasing the chance of scale formation. At  $K_e = 1$ , magnetisation has no effect as equilibrium exists in the solution and there will be no transfer of CO<sub>2</sub> from the combined state to the free state or vice-versa.

The presence of oxygen in the water has an adverse effect on scale prevention because it can react with organic matter (oxidation of carbon to CO<sub>2</sub>) present in the water. As the carbonic acid content in the water builds up there is a greater chance of it combining with Ca<sup>2+</sup> and Mg<sup>2+</sup> to form more scale.

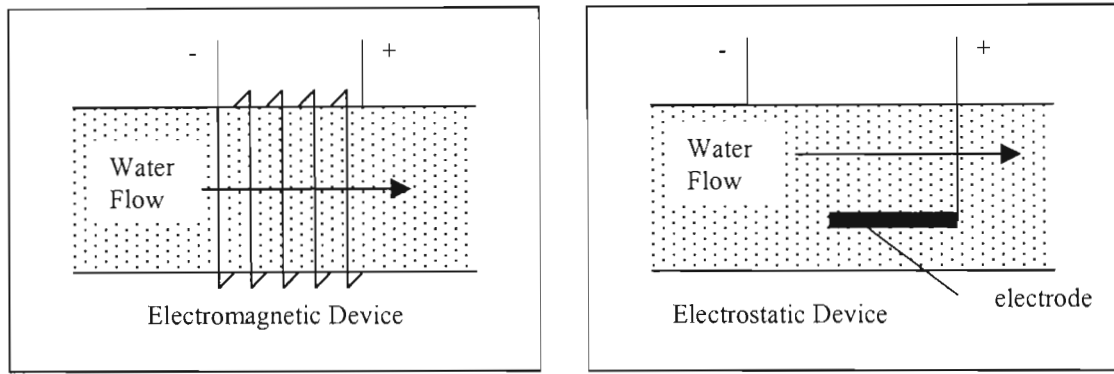
### Types of Magnetic Units

Magnetic units are available in two installation variations and three operational variations. The units may either be installed as invasive or non-invasive. Invasive devices are those, which have part or all of the operating equipment within the flow field. Therefore a section of the pipe would have to be removed for the insertion of the device. Non-invasive devices are completely external to the pipe, and thus can be installed while the pipe is in operation. Fig. 2.4 shows the two installation variations.



**Fig. 2.4 – Variations in Installation of Magnets [33]**

The operational variations include the magnetic (permanent magnet), the electromagnetic (where the magnetic field is generated via electromagnets), and the electrostatic (where an electric field is imposed on the water flow, which serves to attract or repel the ions and, in addition, generates a magnetic field). Electrostatic units are always invasive whereas, the other two types can be either invasive or non-invasive (Fig. 2.5).



**Fig. 2.5 – Non-Permanent Magnetic Devices [33]**

A U.S.-based magnet vendor (GMX) made the following comparisons (Table 2.4) between their magnetic device and the common chemical water softener for a household water system [16]:

Complete GMX System	Salt Based Water Softener
Cost: \$522 to \$696. There are no hidden costs.	Cost: \$1000 to \$2000 or more + \$200 to \$500 for the reverse osmosis unit required to remove the salt from the drinking water.
Feel cleaner and fresher after bathing.	Feel slippery and unnatural and can irritate sensitive skin.
Retains healthful minerals.	Eliminates healthful minerals.
Legal to use in all areas of the U.S.	Outlawed in many communities in the U.S.
Requires no salt and no ongoing expenses.	Requires over 800 lb of salt each year.
Compact and easily self-installed – no tools required.	Requires expensive professional installation - \$200 or more.
Requires no plumbing modifications.	Household plumbing must be modified.
Maintenance free.	Requires constant maintenance and attention.
No back-flushing and no inconvenience.	Interrupts household water flow during back-flushing and mineral regeneration.
Requires no electricity.	Motors and timers consume electricity.
Requires no water.	Uses large amounts of water during back washing.
Silent	Noisy
Improves water flow and pressure by removing scale build-up from inside pipes and appliances.	Reduces normal water flow and pressure.
Does not corrode water heaters, pipes and fixtures.	Can corrode water heaters, pipes and fixtures and lead to expensive repairs.
Prevents and removes existing lime and scale build-up.	Does nothing to eliminate existing lime and scale build-up.
Does not harm the environment or our fresh water supply.	Pollutes waterways; hinders septic systems and waste water treatment programs.
Household plants and lawns thrive.	Damages household plants and lawns.
Safe for heart patients and those with hypertension.	Should not be used by heart patients and those with hypertension.
120-day, unconditional, 100% money back guarantee and lifetime warrantee.	No money back guarantee and finite warrantee period.
Easily take with you when you move (portable).	Leave water softener behind – buy new one.

**Table 2.4 – Comparison Between Magnetic Treatment and Chemical Treatment for a Household System [16]**



## 2.4 Previous Laboratory Studies

Glushchenko and Grishaenko [11] used the following equation to determine the amount of scale build up,  $G'$  ( $\text{g}/\text{m}^3$ ), on heat exchange surfaces in a specific time  $t$  (hr).

$$G' = 3 + 69^{t-0.75} \quad [2.4]$$

Sandulyak and Krivtsov [50] performed experiments on a “tube-in-tube” type heat exchanger. The treated water was circulated through the annular channel between the tubes. Sections of the tubes had flanged connections and were removed in order to measure the amount of scale formed,  $G$  (mg), in the tubes. Results showed that the rate of increase in the amount of deposits  $dG/d\tau$  obeys an exponential function of the type:

$$\frac{dG}{d\tau} = A\tau^{-m} \quad [2.5]$$

where  $\tau$  is dimensionless time ( $\tau = \tau/\tau_r$ ,  $\tau_r = 1$  hour) and  $A$  and  $m$  are coefficients depending on the quality of the water, the parameters of magnetic and thermal treatment and the condition of the heat exchange surface.

In order to establish the effectiveness of the magnetic water treatment, Sandulyak and Krivtsov [50] defined a coefficient of reduction of deposits as:

$$\eta = \frac{\left(\frac{dG}{d\tau}\right)_1 - \left(\frac{dG}{d\tau}\right)_2}{\left(\frac{dG}{d\tau}\right)_1} \quad [2.6]$$

where the subscripts 1 and 2 denote without and with magnetic treatment respectively.

After various experiments it was found that the effect of the heat load ( $q'$ ) on the reduction of deposits obeyed the empirical formula:

$$\eta = \frac{1.9}{\bar{q}'} \quad [2.7]$$

where  $\bar{q}' = q' / q'_r$ ,  $q'_r = 1 \text{ kW/m}^2$ .

$q'$  = heat load of the heat exchanger ( $\text{kW/m}^2$ )

One of the important factors affecting the intensity of carbonate deposit formation in any heat exchange equipment during magnetic water treatment is the specific heat load of the heat exchange surfaces ( $q'$ ). Sandulyak and Krivtsov's [50] laboratory investigations showed that for an evaporation circuit, with a reduction in  $q'$ , the relative reduction in the amount of deposits ( $\eta$ ) increased. Therefore antiscale

magnetic treatment is more effective for heat exchangers with a relatively low heat load. It was also observed that under equal conditions, the value of  $\eta$  in the evaporation circuit was greater than in other heat exchangers.

They also found that the heat load applied to the heat exchanger and the water velocity could not be shut down at the same time because the amount of scale deposited ( $G$ ) increased by 10-20 mg owing to intense boiling of the immobile liquid in the annular channels. There was no flow of the water and the amount of heat that was absorbed by the water was sufficient to cause the water to boil removing carbon dioxide gas and evaporating the water. This concentrated the calcium carbonate and eventually precipitated it out of solution. Therefore the water supply was stopped 5-6 minutes after the shutoff of the heating elements.

Sandulyak and Krivtsov [50] also investigated the effect of water velocity in the zone of the magnetic treatment on  $\eta$ . A graph of  $\eta$  as a function of water velocity showed that a maximum occurred at a certain velocity. In addition to this various diameters of the tube were investigated. It was found that the maximum  $\eta$  shifted towards lower values of velocity when diameter was increased. Since magnetic treatment of water was dependent on the diameter of the tube as well as the velocity of the water, it was concluded that the hydrodynamic criterion of magnetic treatment of water was the Reynolds number ( $Re$ ) and not the velocity. It was found that the optimum values of  $Re$  lied between 2 000 to 3 000 and 9 500 to 10 500, which was in the region of transitional mode of water movement. From the above  $Re$  range, it was concluded that there was only limited efficiency of magnetic water treatment in

the laminar flow region; a certain turbulisation of the water stream was required in order for intense formation of centres of crystallisation; however at a developed turbulent flow a competing factor came into play - disruption of the already formed centres of crystallisation owing to fluctuations in pressure and velocity in the water stream. Therefore the transitional region was considered to be the optimum.

Das and Misra [6] carried out experiments to test the effectiveness of the magnetic water treatment under Indian conditions. Studies were done in Delhi, Calcutta and Bhubaneswar. Pipelines were connected from an overhead water reservoir to water taps and also to water heaters. Parallel connections were made in the water system. Two cast iron pipes were connected to the parallel connections: one with a magnetic unit and one without it. Results showed that after one year, the pipeline fitted with the magnetic unit was well protected from scale and internal corrosion, whereas the pipe without the equipment was damaged by scale and corrosion. The water heater, which was corroded very badly previously, was now cleared. The solid material attached to the heating surfaces became loose and fell off.

Results of laboratory experiments performed by Glushchenko and Grishaenko [11] indicated that the optimum magnetisation conditions were that the field strength be between  $16$  and  $20 \times 10^4$  A/m and the liquid flow rate through the magnetic field be between  $0.4$  and  $0.5$  m/sec. In their experiments the maximum effectiveness was obtained at a field strength of  $16 \times 10^4$  A/m. Composition studies were performed on the scale formed which showed that the scale contained  $83$  to  $85\%$   $\text{CaCO}_3$ . Chemical analysis showed that during magnetisation at  $45^\circ\text{C}$  and above the calcite transformed

almost entirely to aragonite, which gave a less tenacious deposit, whereas under normal conditions a scale layer rapidly built up under these conditions.

## **2.5 Successful Applications of the Magnetic Water Treatment**

Magnetic treatment has many applications such as in buildings, boilers, seawater treatment, oil industry, and oil wells.

Advantages of the magnetic water treatment in certain applications include reduction of scale formation in steam boilers; more efficient removal of solid matter from water (purification processes); more effective extraction of valuable metals from ores; faster solidification of certain cements and increase in the density and strength of casting forms.

A survey of the available literature data suggested several possible areas of magnetic treatment to water purification technology: water pipes and equipment; intensification of crystallisation and coagulation processes; improving the bactericidal effect of disinfectants; and accelerating the effectiveness of utilising ion-exchange resins [39].

Whittle & Turner Ltd. of Kirkham, Lancs [8], gave an example of the successful application of magnetic water treatment. After installation of a unit to their boiler system they made annual savings of about £1 800 in labour costs, fuel, etc., for an outlay of about £250 for the magnetic device. However, it is admitted that these savings are higher than normal considering that the firm used no treatment previously,

although, favourable results have been reported in nearly every case in the UK, where magnetic treatment devices have been fitted.

Magnetic units were attached to suction dredges at the Karakum Channel [55]. Scale in the water jackets of the internal combustion engines were eliminated completely, which in turn, had a positive effect on the stability of the temperature regime.

Taffe [54] gave two other excellent examples of the beneficial effects of the magnetic water treatment. The first example was of a brewery of McMullens & Sons that experienced extensive scaling in a 28 800-gallon hot water storage tank and two heat exchangers. As a result of the implementation of a magnetic unit the amount of acid used annually for descaling decreased from 2 400 litres to 800 litres and the time spent cleaning was reduced by two thirds.

The second example was at the Bedford van plant in Luton. The scale that was originally 6 to 8 mm thick on the walls of a tank of 163 m<sup>3</sup> capacity and weighed about 1.25 tons, was removed on magnetic treatment of the water with estimated annual savings of £22 000.

The driving force of magnetic water treatment is the cost savings that magnetic treatment offers by reducing scale and the inevitable downtime that goes with it.

The above are only a few examples of the successful application of magnetic water treatment, but there are many more. Thus the installation of magnetic units in industry is continuing to grow.

## 2.6 Possible Theories

The mechanism of the effect of the magnetic field on the characteristics of a water system has so far not been fully revealed. Attempts at laboratory modelling of the conditions of industrial use of magnetic units have, in the majority of cases, been unsuccessful.

Investigations show that with certain water chemistry and temperature conditions magnetic units may generate seed crystals. Deposition of scale onto these crystals competes with deposition on the heat transfer surfaces where sludge is effectively removed. Required conditions for crystal formation are that the water is supersaturated with respect to scale forming substances and that the water contains substances with ferromagnetic properties. However, the mechanisms of the crystal generation are not understood and have not been studied exhaustively [44].

It has also been shown that currents and voltages are produced when conducting solutions are passed through a magnetic field with the field being orthogonal to the fluid flow. It has been postulated that the electrolysis products, which result from this process, could be involved in causing preferential precipitation of calcium carbonate in the bulk of the solution rather than on plumbing surfaces. This hypothesis is still being tested [38].

After a number of years of laboratory studies, Donaldson [54] tried to explain the results. He considered three factors - turbulence, the Lorentz effect and crystal nucleation modification.

The Lorentz force is the force exerted on a charged particle and is given by:

$$F = qv \times B \quad [2.8]$$

where,  $q$  = charge of the particle (coulomb)

$v$  = velocity of the particle (m/s)

$B$  = magnetic flux (tesla)

Conversion: 1 gauss =  $10^{-4}$  tesla

tesla = N/A.m

Donaldson [54] found that the effects of turbulence were secondary to the major influence of the magnetic field on the precipitation process. He also considered that the Lorentz effect is not the major effect responsible for the observed phenomena of the magnetic treatment. However, all the data observed thus far could be explained in terms of the modification of crystal nucleation by the magnetic field.

There are three components of the fluid that are affected by the magnetic field: the charged surfaces of the growth nuclei, the anions and the cations. Donaldson [54] concluded that it was in the solid/fluid interface region that explanations of the effects of magnetic treatment of fluids should be sought [54]. However, he could not find these explanations.

Raisen [49] reported that another possible mechanism was based on the principle of magnetohydrodynamics (MHD). The energy acquired by the solids through the MHD effect increases their surface energy and solubility and decreases the particle size.



Water contains charged particles that are energised by the magnetic field due to their motion (their momentum). The interaction of the charged particles with the magnetic field slows the particle. So the energy ultimately comes from the pump that has to work harder to pump the fluid in the presence of the magnetic field.

Since the particles are present in a low concentration very little total energy is absorbed. However the effect of this energy is great since a large amount of energy is absorbed per particle. Thus a large amount of energy is required to solubilise them.

Since the particle concentration and saturation is low, the precipitation process is slowed down and large well-ordered crystals are formed, which have low surface energy relative to smaller particles. As a result small particles with high surface energy, in accordance with Le Chatelier's principle, will tend to form larger particles with lower energy. However, since the magnetic field increases the energy of the smaller particles and causes them to remain small and highly soluble their tendency to form a precipitate is greatly reduced. If scale already exists the small particles will give up some of their energy to the scale and cause it to dissolve. This is a slow process since the energy carrying particles are present in low concentrations and since more energy is required to dissolve scale in the presence of a saturated solution. The magnetic field induces the scale forming species to either remain soluble and be discharged with the bleed or blowdown in the system, or to form small particles that settle in low velocity portions of the system where they can be easily removed.

Another theory is that the dipolar molecules in the liquid to be treated are polarised as they pass through the magnetic field. Precession of the dipole occurs and they (dipoles) thus have an induced magnetic moment with a field at right angles to the inducing field. Since the substances are saturated by the field, the precession is so complete that each molecule acts as a small magnet having a north and south pole. They arrange themselves north to south and south to north with an alignment the same as the fluid flow. The individual field of the dipoles may then mass together and form a mass liquid magnet with a pole strength sufficient to cause magnetic leakage to occur. The applied magnetic field magnetically saturates the mass liquid between the magnets so that it is magnetically saturated and cannot hold any additional field. As the individual dipoles flow pass the magnets, some of the magnetic flux escapes or “leaks” into the surrounding environment. There would then be a breakdown of the fluid magnet and the homogeneous condition of the field would begin to deteriorate. In some fashion it is thought that this deterioration generates a condition in the substances changing their character to such an extent that deposition will be lessened or stopped and perhaps previous deposits removed [46].

There are numerous other theories for explaining the effects of magnetic fields on fluids. Fluid-Tech International Corporation [10] believes that the effect of the magnetic treatment is a combination of the above theories and many other theories.

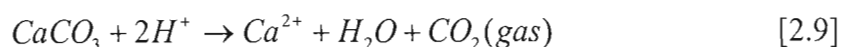
## 2.7 Properties of Calcite and Aragonite

Aragonite and calcite are both forms of calcium carbonate ( $\text{CaCO}_3$ ). Scale is made up of mostly calcite. Aragonite and calcite are polymorphs (i.e. they have the same chemistry but different structures with different symmetries and crystal shapes). Another structure called vaterite is also a polymorph of calcite and aragonite, making them all trimorphs.

Aragonite has an orthorhombic symmetry, while calcite has a trigonal symmetry and vaterite a hexagonal symmetry. Aragonite has a more compact structure and is composed of triangular carbonate ion groups ( $\text{CO}_3^{2-}$ ), with the three oxygen atoms located at the corners of a triangle and the carbon atom at the centre. The carbonate ions lie in two planes that are perpendicular to each other. In calcite the carbonate ions lie in a single plane pointing in the same direction giving it the trigonal symmetry.

Aragonite is unstable at normal temperatures and pressures. It is stable at higher pressures but not at higher temperatures. However, under certain conditions of formation, the crystallization of calcite is discouraged and aragonite will form instead. Some of these conditions include the magnesium and salt content of the crystallizing fluid, the turbidity of the fluid and the time of crystallization. After a given amount of time the aragonite will almost certainly change to calcite.

A simple test for calcium carbonate is the Acid Test. When cold dilute HCl is placed on specimens, calcium carbonate will always effervesce. The reason for the bubbling is in the following reaction:



While the calcium dissolves in the water, the carbon dioxide gas is given off as bubbles. The Acid Test helps to differentiate between calcium carbonate and other carbonates, but does not differentiate between aragonite and calcite. The use of X-ray diffraction and/or the electron microscope may be used for this differentiation.

The differences in the physical characteristics of calcite and aragonite may be seen in Table 2.5 below, the main difference being that calcite is hard like ice whereas aragonite is loose like snow and does not have the ability to form solid lime scale [20, 21, 32].

At room temperature the solubility of aragonite is 0.0012g per 100g of water, whereas that of calcite is 0.0014g per 100g of water.

	<b>Calcite</b>	<b>Aragonite</b>
<b>Colour</b>	White or colourless or with light shades of yellow, orange, blue, pink, red, brown, green, black and grey	White or colourless or with shades of red, yellow, orange, brown, green, or blue
<b>Luster</b>	Vitreous to dull	Vitreous to dull
<b>Transparency</b>	Transparent to translucent	Transparent to translucent
<b>Crystal System</b>	Trigonal	Orthorhombic
<b>Crystal Habits</b>	Common crystals are the scalenohedron, rhombohedron, hexagonal prism, and pinacoid. Combinations of these and over 300 other forms can make a multitude of crystal shapes, but always trigonal or pseudo-hexagonal. Twinning results in crystals with blocky chevrons, right angled prisms, heart shapes or dipyrarnidal shapes.	Include twinned hexagonal prismatic crystals. Also thin elongated prismatic, curved bladed, steep pyramidal (spiked) and chisel shaped crystals. Can have a branching tree, coral or worm like form. Can also be compact, granular, radially fibrous and massive. Its massive forms can be layered, coralloid, globular and stalactitic.
<b>Cleavage</b>	Perfect in 3 directions, forming rhombohedrons	Distinct in one direction (pinacoidal)
<b>Fracture</b>	Conchoidal	Subconchoidal
<b>Hardness</b>	2.5 – 3	3.5 – 4
<b>Specific Gravity</b>	2.7	2.9
<b>Streak</b>	White	White
<b>Other Characteristics</b>	Refractive indices of 1.49 and 1.66 causing double refraction effect. Effervesces easily with dilute acids and may be fluorescent.	Refractive index = 1.7. Effervesces in cold dilute HCl; strongly birefringent; fluorescent.

**Table 2.5 – Physical Characteristics of Calcite and Aragonite [20, 21]**

## 2.8 Hardness of Water

Hardness is a measure of the amount of dissolved ions in the water. The primary ions are calcium and magnesium while iron and manganese may also play a role.

For a solution containing only calcium carbonate, hardness is measured by the amount of calcium present in the water (in terms of ppm). Table 2.6 gives a brief description of the different ranges of ppm of calcium carbonate.

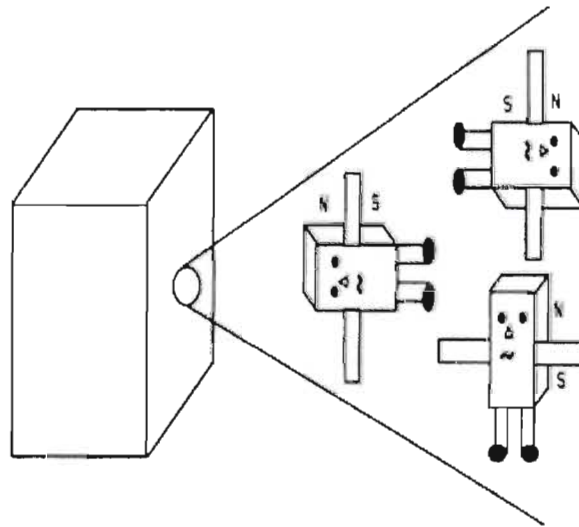
<b>Concentration (ppm CaCO<sub>3</sub>)</b>	<b>Description</b>
0 - 75	Soft
75 - 150	Moderately hard
150 - 300	Hard
300 and up	Very hard

**Table 2.6 – Classification of Water by Hardness Content [22]**

## 2.9 Magnets and Magnetic Fields

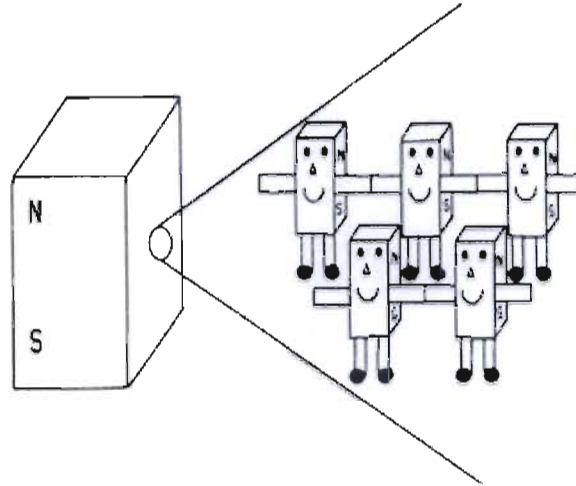
Magnetic fields are produced by the motion of charged particles. Therefore electrons flowing in a wire will produce a magnetic field surrounding the wire. The electromagnet is constructed from many coils of wire wrapped around a central iron core. The magnetic field is only present when current is flowing through the wire of the coils.

The magnetic field of a permanent magnet results from the mutual alignment of the very small magnetic fields produced by each of the atoms in the magnet. These atomic-level magnetic fields result mostly from the spin and orbital movements of electrons. When the permanent magnet is demagnetised (either by heating to the Currie Temperature or cycling it in a magnetic field) each atomic moment points at random (Fig. 2.6) and no net force is observed.



**Fig. 2.6 – Demagnetised Permanent Magnet [29]**

When a permanent magnet is magnetised in a strong magnetic field all the atomic moments are aligned to the same direction and once there, are held in ‘lock-step’ with each other (Fig. 2.7), which allows the magnet to retain its magnetism on removal from the magnetic field and also resist the effect of a field applied in the reverse direction.



**Fig. 2.7 – Magnetised Permanent Magnet [29]**

The atomic moments add up to produce a total magnetic moment for the permanent magnet, and the magnetisation,  $M$  is the total magnetic moment per unit volume. The strength of a magnet is given by its magnetic flux density (measured in units of gauss). This is the result of the driving force of the externally applied magnetic force,  $H$  and that from the internal magnetisation,  $M$ . The earth's magnetic field is of the order of 0.5 gauss. On an area independent basis, the flux density of a magnet is given by:

$$B = \mu_0 (H + M) \quad [2.10]$$

where,  $B$  = magnetic flux density (T)

$\mu_0$  = permeability of free space ( $4\pi \times 10^{-7}$  T.m/A)

$H$  = externally applied magnetic force (A/m)

$M$  = magnetisation (A/m)

Conversion:  $1 \text{ G} = 10^{-4} \text{ T}$



Magnetic field lines are imaginary lines that show the direction of the magnetic field and always flow from the north pole to the south pole of the magnet as illustrated by Fig. 2.8.



**Fig. 2.8 – Magnetic Field Lines for a Bar Magnet [24]**

## CHAPTER 3

### EXPERIMENTAL

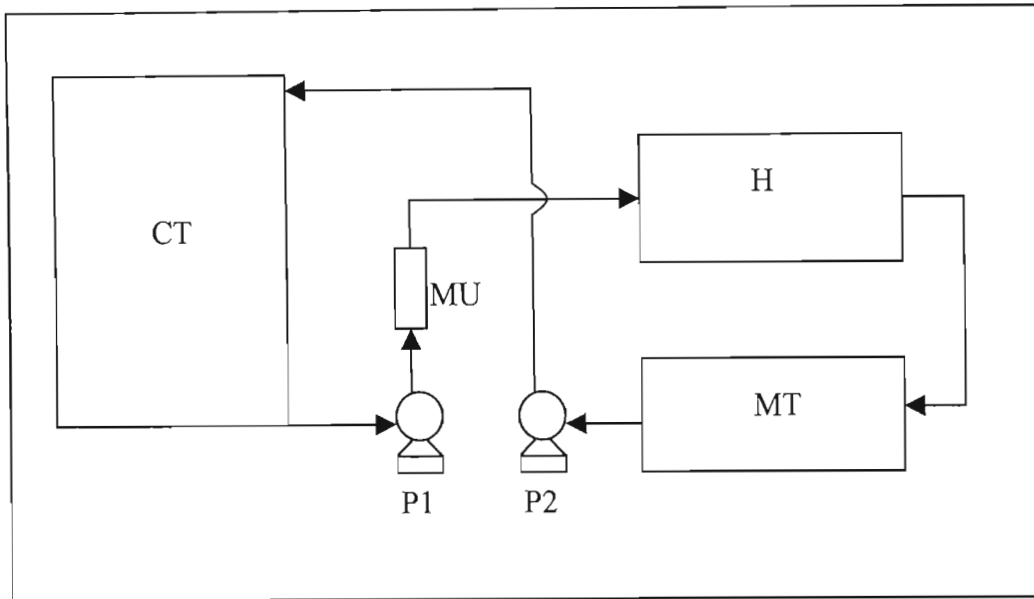
#### 3.1 Initial Experimental Setup

The concept behind the initial setup was to test water properties (with and without the magnetic treatment) in a system that heated and cooled the water continuously as heating and cooling changes the physical properties of the water.

The basic components of the experimental heat exchange system were:

1. a magnetic unit (MU),
2. two pumps(P1,P2),
3. an electrical heating unit (H),
4. a mixing tank (MT),
5. a cooling tower (CT), and
6. a network of pipes connecting the components.

A flow diagram is provided in Fig. 3.1 below.



**Fig. 3.1 - Flow Diagram of Initial Experimental System**

The magnetic unit was made up of a pair of permanent magnets situated opposite each other in order to create the required magnetic flux. The heating unit had 3 x 3 sets of elements of 3 kW each to give a total power capacity of 27 kW that was needed to heat the water to between 65 and 75°C. The dimensions of the heating unit were 600 x 300 x 750 mm. The mixing tank had a capacity of 75 litres with dimensions of 400 x 300 x 750 mm. The purpose of this unit was to bring the temperature down to approximately 50°C. The mixing tank also served as a means to introduce corrosive salts and other chemicals into the water line. The cooling tower, with dimensions of 556 x 700 x 1720 mm, used evaporation in order to bring the water down to ambient temperature. Pump P1 was required to pump water from the cooling tower sump to the heater unit. Pump P2 was required to pump the water from the mixing tank up to the cooling tower. The piping network had a diameter of 25.4 mm and was constructed of copper.

The pipe from the cooling tower to the heater unit consisted of three 100 mm sections while the pipe from the mixing tank back to the cooling tower consisted of five 100 mm sections that were attached to each other by flanges. The advantage of this was that a section could be removed and tested for scaling and corrosion, while a new one replaced the removed section. This allowed each of the sections to be tested according to a time sequence devised by the researcher.

A method to test the efficiency of the magnetic water treatment, as stated by Vermeiren [56], is to pour 200 ml of treated and untreated water in two separate beakers. A glass slide is placed in each and boiled for 30 minutes. Precipitation of calcium carbonate and other salts will begin sooner in the treated water, with these precipitates adhering less to the sides of the beaker that remains clearer. The two slides are then removed from the beakers, dried at 110°C and compared under the microscope.

This system proved to have too many variables and, as a result of inconclusive results being obtained, it was decided that a simple bench-top system be built with the cooling system being eliminated. The precipitation of calcium carbonate increases with temperature (solubility decreases), therefore, only a means of heating the water and maintaining it at a constant temperature was required.

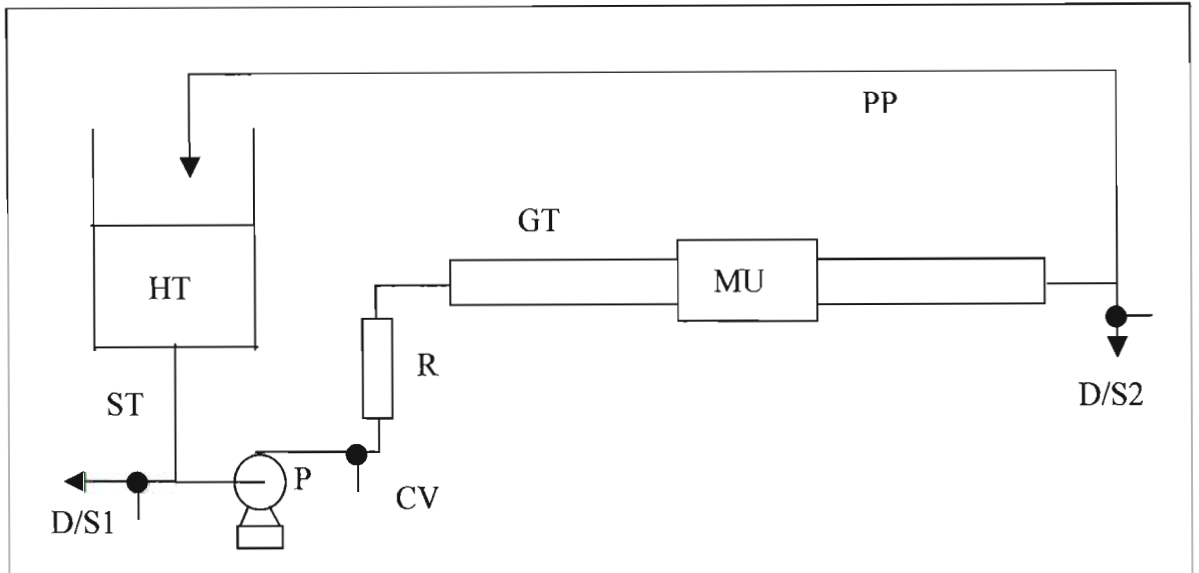
### 3.2 Preferred Experimental Setup

The second (preferred) setup, which was used to run the experiments that are reported in this thesis, was a bench-top system with a heating system and a means to recirculate the water.

The basic components of the heat exchange system were:

1. a glass tank (fitted with heating elements on the outside) (HT)
2. a small centrifugal pump (P)
3. a rotameter (R)
4. a two meter long, 25.4 mm glass tube (GT)
5. the magnetic unit (MU)
6. polycorp pipe (PP)
7. silicon tubing to complete the piping network (ST)
8. drain / sample points (D/S)
9. a flow control valve (CV) and drain valves
10. absorption spectrophotometer
11. flow cell for the spectrophotometer to make readings online
12. peristaltic pump
13. pH meter

A flow diagram of this experimental rig is shown in Fig. 3.2 below, while a photograph is provided in Fig. 3.3.



**Fig. 3.2 – Flow Diagram of Preferred Experimental System**



**Fig. 3.3 – Photograph of Preferred Experimental System**

### 3.2.1 Equipment Specifications and Selection

The heater tank (Fig. 3.4) was a ten-litre glass vessel that had an exit point at the centre of the bottom surface. The system was open to atmosphere. The tank was fitted with a heating element that formed three coils around the outside of the tank. The elements were chosen to fit onto the outside rather than in the water in order to eliminate the effect of the element on the properties of the water. Furthermore, calcium carbonate deposits may have formed on the surfaces of the elements (if inserted in the water) and thereby may have reduced the heat transfer, making cleaning difficult as well.



**Fig. 3.4 – Photograph of Heater Tank**

The elements were connected to a single set point temperature controller (Zenith Model 72T) that had an analogue setting. A thermostat, connected to the controller was inserted into the tank. The controller thus allowed the elements to heat the solution to the desired temperature and maintained it there.

Literature stated that the flow through the magnetic unit should be in the laminar or transitional regime and not in the turbulent regime [10,50]. The flow needed to be constant and as a result, a centrifugal pump was required to maintain a low, constant flow rate. The pump that was used was a small “fish tank” pump (230V, 50Hz, 0.6A, single phase) that produced a maximum flow rate of 250 l/hr. For laminar flow in a pipe, Reynolds number must be less than 2 300. A flow rate of 150 l/hr was chosen which is equivalent to a velocity of 0.082 m/s. In a 25.4 mm ID pipe, the Reynolds number calculated was 2 083. This flow rate was used as a basis for most of the runs. A manual flow control valve (CV) located between the pump and the rotameter was used to regulate the flow.

The rotameter had a maximum flow reading of 1 000 l/hr. Rubber hosing of 9 mm ID was used to connect the heater tank to the pump, the pump to the rotameter and the rotameter to the glass tube.

The glass tube was 2 m long with an inside diameter of 25.4 mm (Fig. 3.5). A long piece of pipe was required in order reduce the end effects of flow and to ensure that the solution passing through the magnetic unit could be in the laminar regime. Glass was chosen for the pipe and the heater tank in order to observe exactly when



precipitation started and also have a visual indication of how fast the precipitation process was taking.



**Fig. 3.5 – Photograph of the Glass Tube Showing the Magnets**

The magnets were Eneflow 1 000 flow dynamic power cells. The magnets had dimensions of 60 x 130 mm and were clamped opposite each other on the glass tube.

Poycorp pipe (19 mm) together with copper 90° bends were used to complete the circuit i.e. to connect the glass tube to the heater tank. The entire structure was built on a metal frame.

A Hanna pH212 microprocessor pH meter was used to measure pH and temperature. The probes were inserted into the tank and measurements were taken at constant time intervals.

An Ultospec 1000E spectrophotometer was used to measure the absorbance of the solution in the tank at different time intervals. A flow cell was used in the spectrophotometer in order to make measurements online. A tube was inserted into the tank and sent to the spectrophotometer via a peristaltic pump. The solution was then returned to the tank through another tube. Using this method, the actual absorbance of

the solution in the tank could be measured and this gave an indication of the precipitation rate.

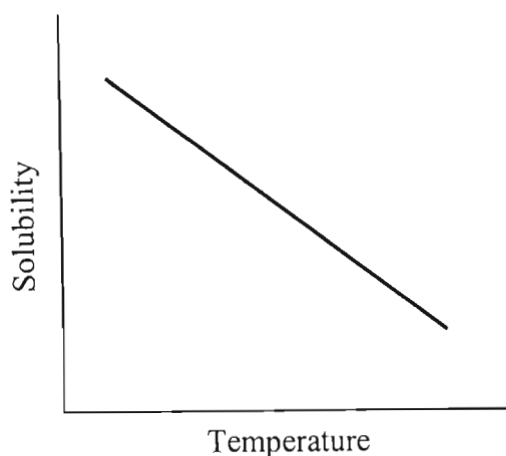
### 3.2.2 Feed Preparation

Scale normally takes a long time to form (months/years) and in order to perform experiments on the calcium carbonate precipitate the scaling process had to be accelerated.

The immediate cause of scale formation is the deposition of a precipitate (mainly calcium carbonate) from a supersaturated solution. Factors giving rise to supersaturation are concentration of the solution, temperature and pressure changes and change in pH. When these factors reach limiting values, the dissolved salt nucleate and form crystals, which may occur as water suspended particles or surface scale.

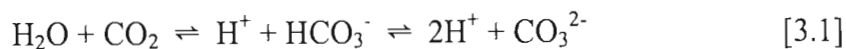
A saturated or supersaturated solution of calcium carbonate was needed as a feed to the experimental system.

Usually, in order to crystallise a salt, a saturated or supersaturated solution is required. As temperature is reduced the salt will crystallise out of the solution. However, this is not the case for calcium carbonate. The solubility of calcium carbonate decreases with increasing temperature (Fig. 3.6). Therefore, once the solution is formed, it will have to be heated in order for the salt to crystallise.



**Fig. 3.6 – Solubility Trend of Calcium Carbonate**

In solution, there exists an equilibrium between the carbonate ion ( $\text{CO}_3^{2-}$ ), the bicarbonate ion ( $\text{HCO}_3^-$ ) and the  $\text{CO}_2$  gas:

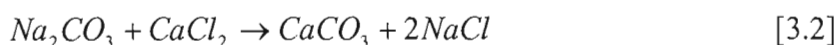


By heating the system, the dissolved carbon dioxide is removed from the solution forcing the carbonate ions out of solution and thus forming calcium carbonate precipitate.

The  $K_{\text{sp}}$  (solubility product constant = [concentration of  $\text{Ca}^{2+}$ ] x [concentration of  $\text{CO}_3^{2-}$ ]) value for calcium carbonate at room temperature is  $4.9 \times 10^{-9}$ , which implies that it is virtually insoluble in water. It just forms a viscous slurry. This makes it difficult to make the saturated solution of calcium carbonate with sufficient amount of the ions dissolved in the solution.

**Unsuitable methods of preparing the feed****Method 1**

As a first attempt appropriate volumes of sodium carbonate and calcium chloride were mixed to form the solution of calcium carbonate according to the following reaction:



Many different volumes of solutions of sodium carbonate and calcium chloride were mixed to try and form the saturated solution. However, as soon as a small amount of one solution was mixed with the other, the calcium carbonate would precipitate out and not stay in solution. The reason for this is the insolubility of calcium carbonate in water at neutral pH. As a result thereof this proved to be an unsuitable method for preparing the feed.

**Method 2**

Although calcium carbonate is insoluble in water, it is soluble in acid solutions. A second attempt for preparing the feed was to mix calcium carbonate in distilled water (approximately 6 g  $\text{CaCO}_3$  in 4 litres of distilled water). Hydrochloric acid was added drop-wise to reduce the pH to approximately 1.9 (approximately 20 ml of 32% HCl). The solution was then neutralised by adding 1M NaOH to bring the pH to 7.0 (approximately 100 ml).

This feed was used for many experiments both with and without the magnets. It was, however, difficult to produce calcite (scale). After X-ray diffraction, the precipitates that were formed both with and without the magnets proved to be essentially aragonite. This was because the solution was in such a state so as to precipitate very quickly. Because aragonite precipitates faster than calcite, aragonite was the preferred precipitate. Therefore this method of producing the feed was unsuitable.

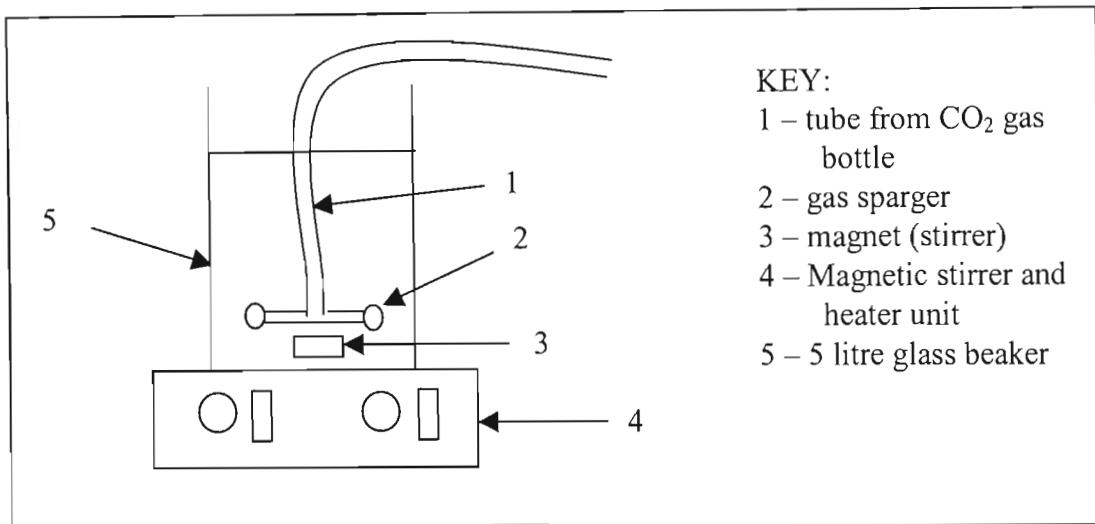
### **Preferred method of producing the feed**

#### Method 3

As a final attempt to produce the feed the calcium carbonate was mixed in distilled water using a magnetic stirrer. CO<sub>2</sub> gas was bubbled through the solution (Fig. 3.7) in order to dissolve the calcium carbonate (approximately 2 g CaCO<sub>3</sub> in 4 litres distilled water) according to the following reaction:



The hardness of the feed was estimated to be approximately 200 ppm. It took more than an hour for the calcium carbonate to dissolve. Using this method for preparing the feed produced fairly good results from the experiments.



**Fig. 3.7 – Preferred Feed Preparation Setup**

This is basically what happens in nature. There is always a balance between the amounts of CO<sub>2</sub>, carbonate ions and bicarbonate ions in solution. The greater the amount of carbon dioxide in solution, the greater the solubility of calcium carbonate. When the solution becomes supersaturated with calcium carbonate (by evaporation of water or increasing the temperature of the solution), the salt will precipitate out, thus forming scale. Therefore this method proved to be suitable for the preparation of the feed in order to simulate an accelerated scaling process.

### 3.2.3 Readings Taken

As stated above a temperature probe and a pH probe was inserted into the heater tank. The temperature remained fairly constant (varying  $\pm 2^{\circ}\text{C}$  from the setpoint). The pH of the solution in the tank was recorded every two minutes for the duration of experiment. The reason for recording the pH was because the precipitation process is

highly dependent on pH and the fact that the pH changes continuously throughout the process.

A tube was run from inside the tank (via. a peristaltic pump), through a flow cell that was in the spectrophotometer and returned back to the tank. Using this setup, absorption of the solution in the tank was recorded every two minutes. The absorption was recorded in order to establish the time taken to start precipitation as well as the precipitation rate. It was difficult to remove samples every two minutes in order to measure the absorption, therefore, this on-line system worked well for recording the absorption timeously.

### **3.2.4 Start-up and Shutdown**

Refer to Fig. 3.2 for the flow diagram of the experimental system.

For the start-up, the flow control valve and drain valves were closed. 3.5 litres of feed, from the feed batch, was poured into the heater tank. The required temperature was set on the controller and the elements were switched on. When the required temperature (setpoint) was reached, a timer was started and the pump was switched on. The flow control valve was opened to allow for the required flow rate. The spectrophotometer was also zeroed and this was taken as the reference.

The system was allowed to run with pH and absorption readings taken every two minutes.

For the shutdown, the pump together with the elements was turned off. Drain valve 1 was opened to drain the solution from the tank. Part of the residue remained in the tank and was rinsed out with distilled water. Drain valve 2 was then opened to drain the solution from the pipes. Once again part of the residue remained on the surfaces of the pipes and had to be rinsed out with distilled water.

Once the system was drained, it had to be cleaned to remove all the residue. HCl was added to distilled water till the pH was approximately 2.0. This solution dissolved the remaining residue from the system and was allowed to run through the system for approximately 30 minutes. Once this solution was drained, the system was again flushed with distilled water for approximately 30 minutes.

### **3.3 Analysis Tests**

The solution, from the experiments, was passed through a filtering system. The precipitate obtained was partially dried during the filtration process and then left to totally dry overnight. Samples of the filtrate were also taken before distilled water was added to rinse the system.

#### **3.3.1 X-ray Diffraction**

X-ray diffraction was performed on the precipitates to identify the constituents of the solid. The test was first done qualitatively to establish exactly what compounds were present and then quantitatively to calculate the proportions of calcite and aragonite in the precipitate. Each sample took approximately one hour to analyse.



### 3.3.2 Atomic Absorption

Atomic absorption was used to test the hardness of the feed and filtrate samples. Once the filtrate was obtained, it was centrifuged to remove all the solid particles. A few drops of nitric acid were added to the samples to prevent any further precipitation. This was done because the samples could not be analysed immediately and after a few days, due to temperature changes of the surrounding, further precipitation may have taken place.

The atomic absorption spectrophotometer was fitted with a calcium lamp. The wavelength was set at 424 nm. The calcium lamp sent a ray of light through the sample and measured the absorption. Using standards of known concentrations, an absorption versus concentration calibration graph was drawn. Using this graph, the concentration of the unknown sample was obtained by measuring its absorbance and finding the corresponding concentration. The concentrations were expressed so as to reflect hardness of the solution in terms of ppm (mg calcium carbonate per litre of solution).

### 3.3.3 Electron Microscope

Samples of the precipitates were chosen to observe under the electron microscope in order to view the crystal structures of the precipitates. Three samples were taken. The first one was pure calcite (commercial grade calcium carbonate); the second was pure aragonite (obtained from one of the experiments with the magnets); and the third was

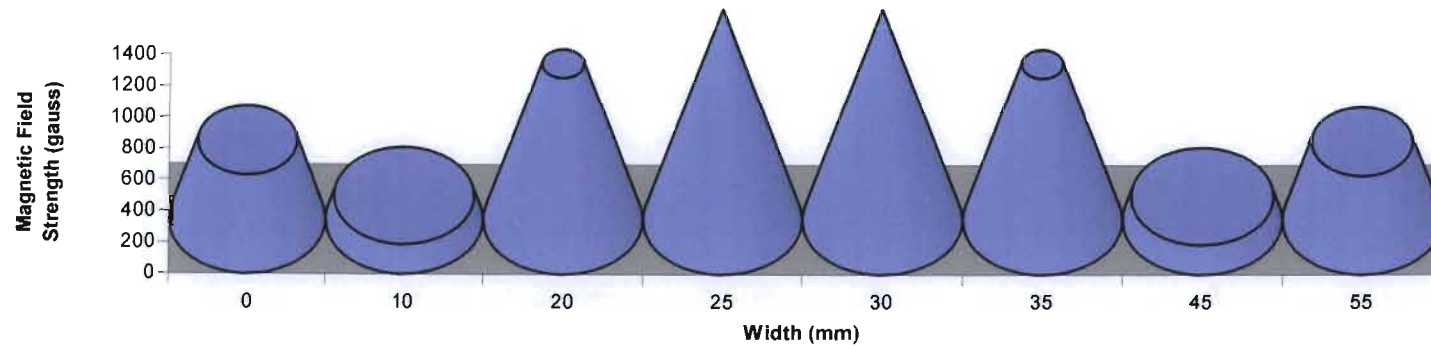
a combination of the two structures (approximately 60% aragonite and 40% calcite (obtained from one of the experiments without the magnets)).

A carbon conducting tape was placed on stubs and the sample was dabbed onto the tape. The sample was then coated with gold (using the Polaron SC500 Sputter Coater) for approximately four minutes. The samples were then placed into the electron microscope (JEOL JSM – 6100 Scanning Microscope) and observed at a magnification of x4 000. Photographs were taken of specific structures.

### **3.4 Magnet Properties**

The magnets were purchased from a local supplier. Unfortunately not much information could be obtained about the magnets.

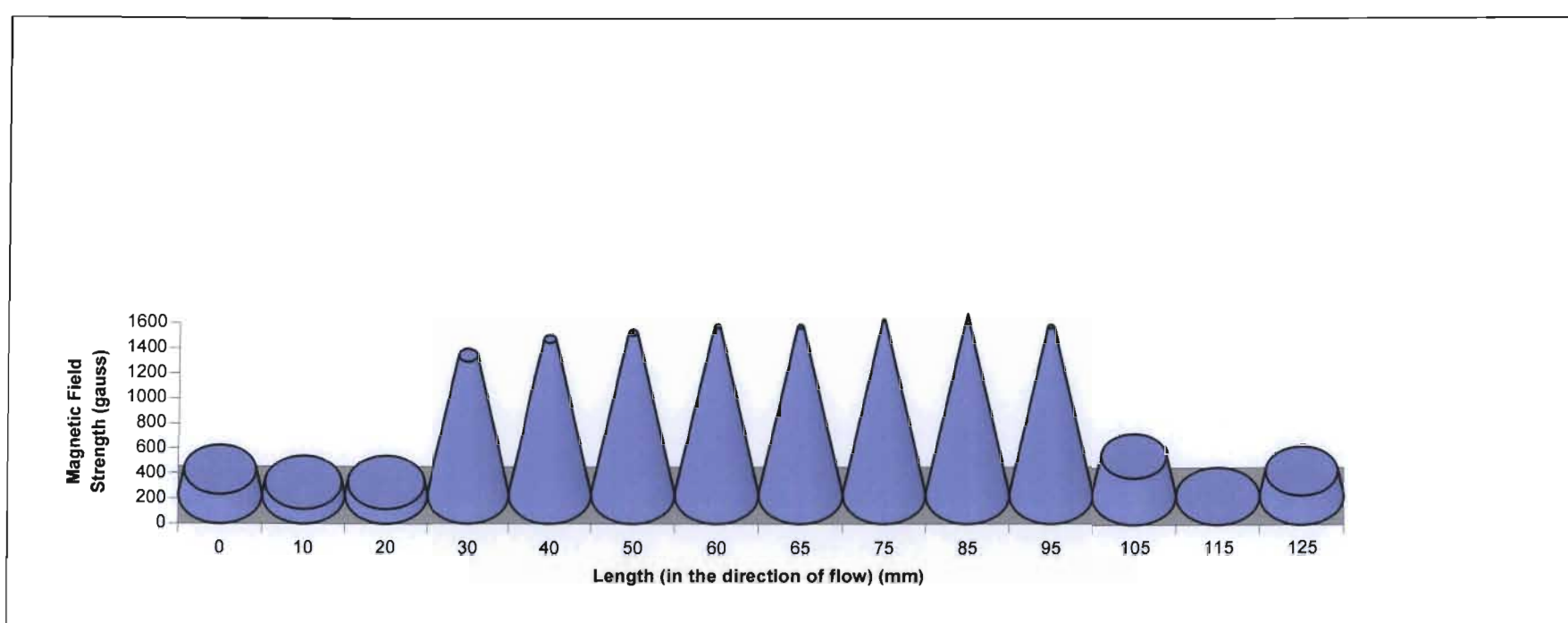
A flux density meter was used to test the strength on the magnets. It was found that both the magnets were identical having a north pole at the centre surrounded by south poles. The flux density changed throughout the length of the magnet, ranging from 0 to 1 450 gauss (Figs. 3.8 and 3.9). Since both magnets were identical and were clamped opposite each other, the magnets repelled each other. Therefore the field strengths were only present at the surface of the pipe (adjacent to the magnet). As a result a gauss magnetic field of zero was measured at the centre of the pipe.



**Fig. 3.8 – Variation of Magnetic Field Strength Along Width of Magnet (centre of length)**

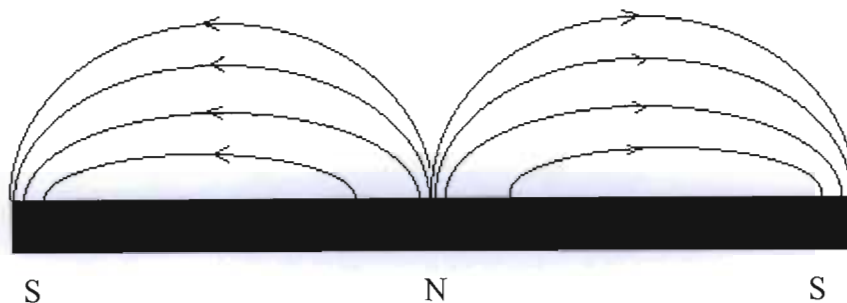
The width of the magnet was 60 mm. It can be seen from Fig. 3.8 that the flux was at its highest value (approximately 1 350 gauss) at the centre of the magnet and slowly decreased to 0 gauss towards the ends. The flux then increased to approximately 0.5 gauss at the end of the magnet. It must be noted that at the end of the magnet (5 mm and 10 mm) a south pole was measured whereas a north pole was measured at the centre.

The length of the magnet was 130 mm. Fig. 3.9 indicates that the flux decreased from approximately 200 gauss to 0 gauss (measuring a south pole) and then increased to a maximum of 1 450 gauss at 85 mm along the length of the meter (measuring a north pole). It then decreased to 0 gauss and increased again to approximately 200 gauss at the end (south pole).



**Fig. 3.9 – Variation of Magnetic Field Strength Along Length of Magnet (centre of width)**

Magnetic field lines always flow from the north pole to the south pole of a magnet. Since the magnets used had a north pole in the centre surrounded by south poles, an estimate of the field lines is as given in Fig. 3.10.



**Fig. 3.10 – Magnetic Field Lines of the Permanent Magnet**

### 3.5 Feed Capacity

The feed tank had a capacity of 10 litres. Initially all runs were run with 8 litres of feed charged to the system. However, it was found that all the solution might not have passed through the magnetic field. Therefore precipitation may have occurred in the feed tank with water that was not magnetized. It was important to know exactly how long it took for the solution to move through the system and what capacity of fluid should be used to ensure that all the fluid passed through the magnetic field.

Refer to Appendix A for the calculation of feed capacity and residence time. It was found that the residence time at a flow rate of 150 l/hr was 50 seconds. Two litres of fluid filled all the pipes (while the tank was empty). Therefore the maximum amount of feed that could be used (to ensure that all the fluid passed through the magnetic field) was 4 litres. Therefore 3.5 litres of feed was chosen as the feed capacity.

## CHAPTER 4

### RESULTS AND DISCUSSION

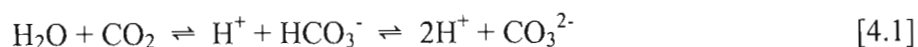
#### 4.1 Initial Results Obtained

Many experiments were carried out using the feed prepared by method 2 discussed in Section 3.2.2. The results are given in Appendix B. Analysis of the precipitates indicated that it was essentially aragonite and very little (if any) calcite. This was the case even when the magnets were not used. As a result, this method of making up the feed was unsuitable.

It was also found that the absorbance graph was not reliable after the precipitation started. When precipitation started (this was observed by the water turning milky) the absorbance started to increase (there were more solids in the water, therefore this was expected). However, when the precipitation stopped and the material was simply settling in the tank and the tubes (this was observed by the water turning clear), the absorbance continued to increase. This was because some of the solids from the solution that was passed to the spectrophotometer adhered to the walls of the flow cell and did not leave with the solution. Therefore, it was found that the absorbance of the tank solution continually increased when it should have been decreasing (since the water was turning clear).

Another important realization was that absorption is used to indicate the concentration of dissolved substances in solution and not solid material (precipitate). Therefore this was not a good means of testing the rate of precipitation. A turbidity meter should have been used instead of a spectrophotometer.

The pH graph was more reliable than the absorption graph. Initially when the temperature was increasing and then when it was constant, the pH was increasing because the increased temperature was driving the carbon dioxide out of the solution. An equilibrium exists between the carbon dioxide and the amount of carbonic acid in the solution as shown in the following reaction:

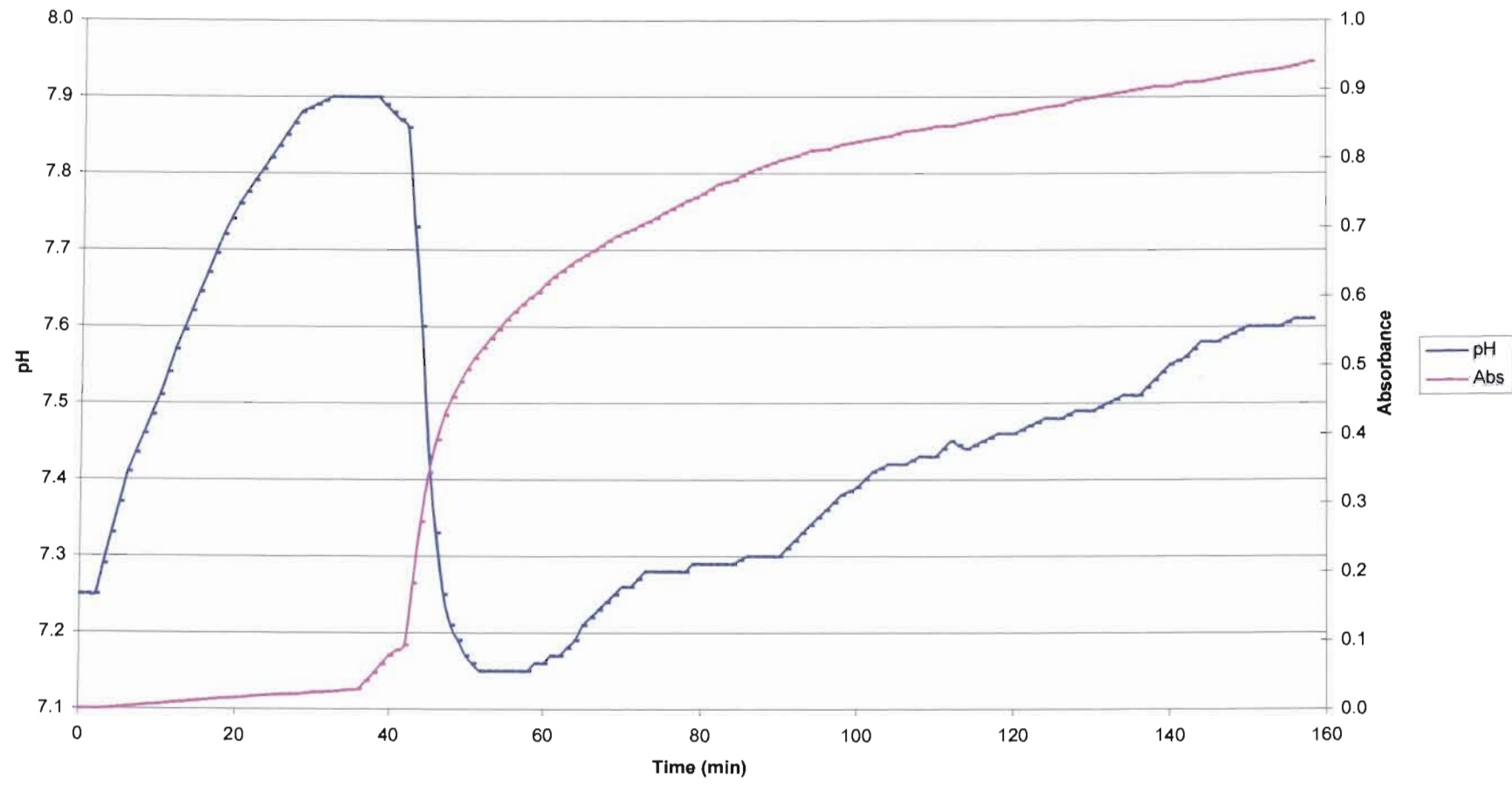


As a result the removal of carbon dioxide reduced the amount of carbonic acid thus increasing the pH. This occurred until the solution became supersaturated with calcium carbonate and precipitation started, which caused the pH to decrease. The reason for the decrease was because  $\text{Ca}^{2+}$  cations and  $\text{CO}_3^{2-}$  anions were being removed from solution as calcium carbonate shifting the above equilibrium reaction [4.1] to the right, producing more  $\text{H}^+$  ions and decreasing the pH.



The pH decreased to a certain point and then leveled off. The probable reason for this is that the rate at which carbon dioxide was being removed was equal to the rate of precipitation of calcium carbonate. When precipitation stopped, or occurred at a slower rate, the pH started to increase again. It was observed that the precipitation had stopped because the solution in the tank and the glass tube started to clear from the top downwards (the solids began to settle). The reason for the increase in pH was because the rate of precipitation was less than the rate at which carbon dioxide was being removed and when the precipitation stopped, carbon dioxide was still being driven off reducing the amount of carbonic acid and increasing the pH. However, the solution was no longer supersaturated and thus did not allow any precipitation to take place.

The pH graph was thus a very good indication of the calcium carbonate precipitation process that occurred in the system. Fig. 4.1 below shows a correlation of pH and absorbance for one of the experiments.



**Fig. 4.1 – Correlation between pH and Absorbance**

More graphs may be viewed in Appendix D to show the repeatability of the pH/absorbance correlation. In this particular experiment eight litres of feed was placed in the heater tank and heated to 60°C. The pump was started and the solution was allowed to circulate in the system for approximately three hours.

It can be seen from Fig. 4.1 that there was a fairly good correlation between pH and absorbance. The pH increased initially while the absorbance remained zero. There was no change in the absorbance of the solution because there was no precipitation, but carbon dioxide was being driven off, resulting in an increase in the pH. When precipitation started the pH dropped and the absorbance increased (the water turned milky). This occurred after approximately 40 minutes. When precipitation stopped after approximately 60 minutes, the pH started to increase. It was from this point that the absorbance graph became unreliable. The absorbance should have leveled off and then decreased continuously, but as explained above it continued to increase.

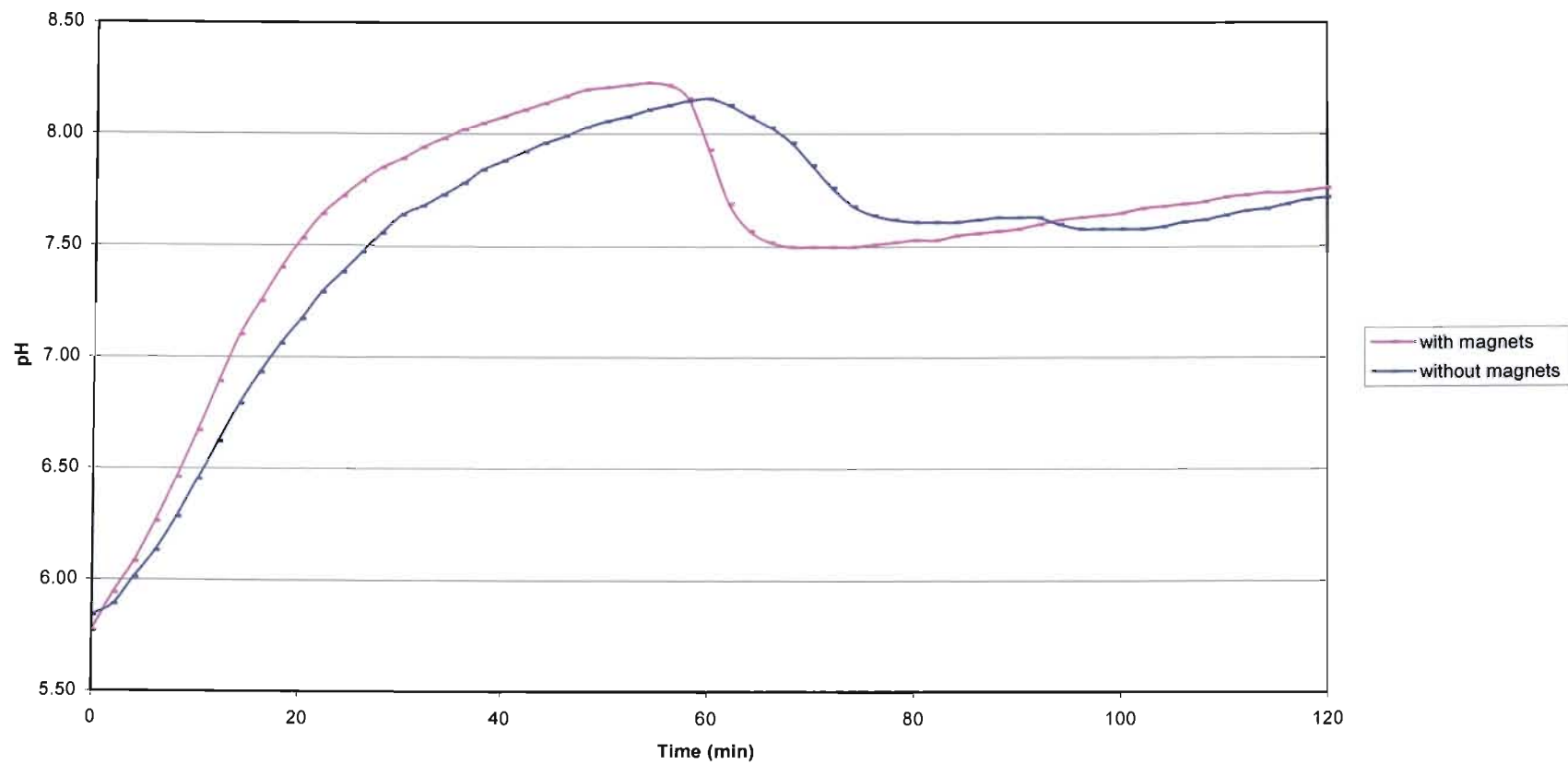
After many experiments, the measuring of absorbance of the solution was abandoned and only pH was measured. All the useful information was obtained from the pH graph including the time taken before precipitation started, the time taken for precipitation, the rate of precipitation and the settling time.

## 4.2 Results Obtained with the Preferred Feed (method 3)

The procedure for preparing the feed was to bubble carbon dioxide through a solution of calcium carbonate and distilled water in order to dissolve the solid. Results obtained with this feed were very promising with regards to the effect of the magnetic field on the precipitation process. For the first time it was possible to produce some calcite in the system. The precipitate was still predominately aragonite, but a fair amount of calcite was present when the system was run in the absence of the magnetic field. There was also a clear difference in the pH graphs (for systems with and without the magnets) indicating the difference in the precipitation of calcite and aragonite.

The capacity of the system was recalculated to ensure that all the solution passed through the system (and the magnetic field, when it was used). As a result, 3.5 litres of feed was added to the heater tank for each run.

Fig. 4.2 shows typical trends of pH versus time for the systems with and without the magnetic fields. In this particular experiment 3.5 litres of solution was added to the heater tank and heated to 30°C. The pump was started and the system was run for approximately 2.5 hours.



**Fig. 4.2 – pH Graph for a Temperature of 30 °C**

It can be seen from Fig. 4.2 that there was a clear and distinct difference in the behavior of pH for the systems with and without the magnetic fields. The precipitation with the magnets started before the precipitation without the magnets. It was also apparent that the time taken for precipitation (from the point when pH started to decrease to the point when pH started to increase) for the system with the magnets was much lower than that for the system without the magnets. This is because aragonite forms much faster than calcite. From the slopes of the graphs (during precipitation) it can be seen that the precipitate with the magnets was formed faster than the precipitate without the magnets (characteristic of aragonite).

X-ray diffraction analysis showed that the system without the magnets produced a precipitate that was 40% calcite and 60% aragonite while the precipitate from the system with the magnets contained 4% calcite and 96% aragonite. This showed a clear reduction in the amount of calcite formed by exposing the system to a magnetic field.

The reason for the large amount of aragonite in the precipitate was because the precipitation process was being accelerated and very hard water was being used (approximately 200 ppm). It must also be noted that scale may take months to form under normal conditions and this system was precipitating calcium carbonate in less than an hour. Once again, because aragonite forms much faster than calcite, the acceleration process favored the precipitation of aragonite.

### 4.3 Effect of Temperature

Once it was established that the magnetic field caused a reduction in the amount of calcite that was formed, the effect of temperature on the effectiveness of the magnetic field was investigated.

The system was charged with 3.5 litres of feed and heated to the required temperature. The solution was allowed to circulate in the system while the temperature was maintained at the desired value.

Figs. 4.3 to 4.8 show how pH changed with respect to time for systems, with and without, the magnets at various temperatures. Note that the duration of some of the runs were shorter than two hours, but the scale of the time axis in all the graphs (Figs. 4.3 to 4.8) was kept constant (0 to 120 minutes) so that comparisons could easily be made.

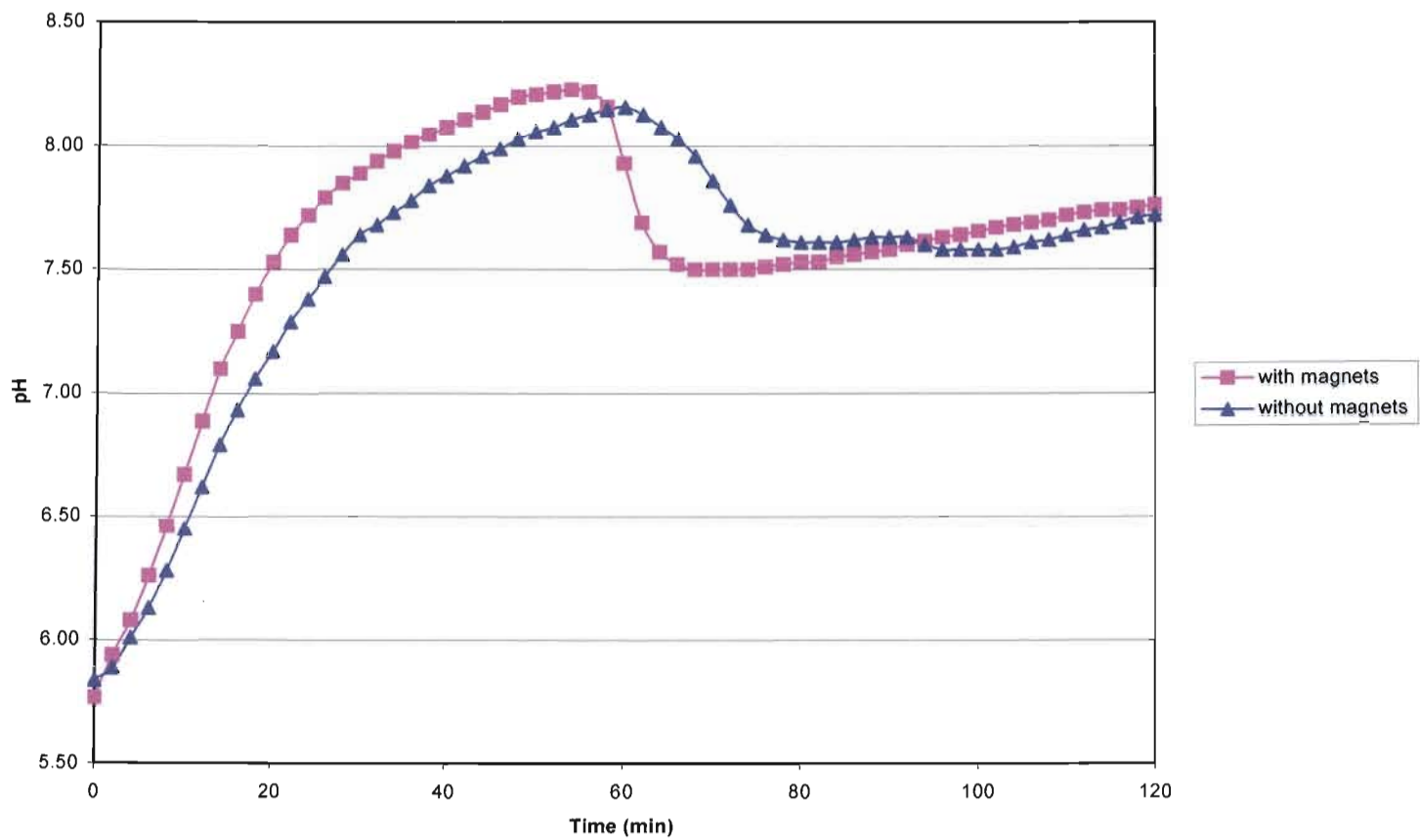


Fig. 4.3 – pH Graph for a Temperature of 30°C



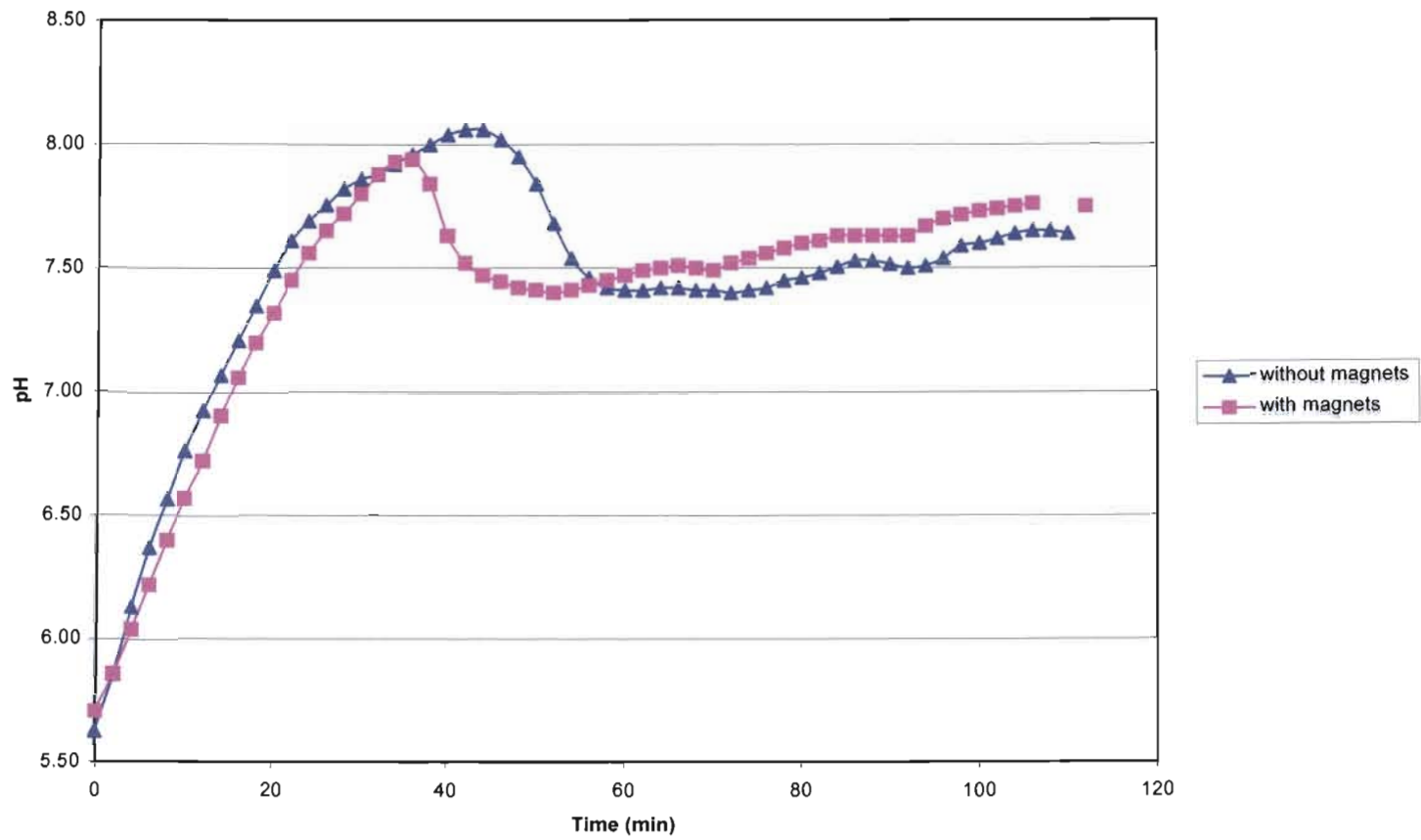


Fig 4.4 – pH Graph for a Temperature of 40 °C

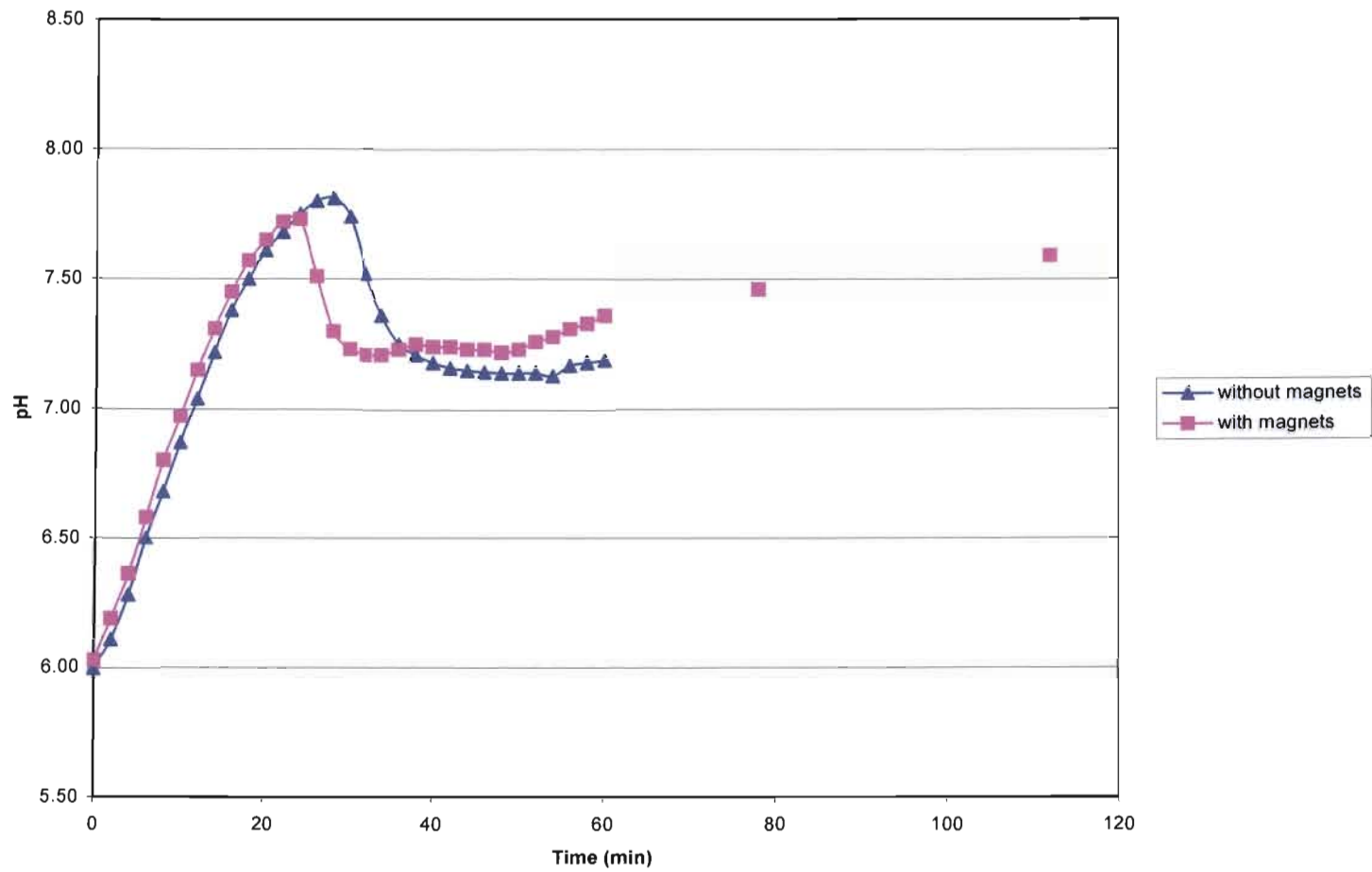
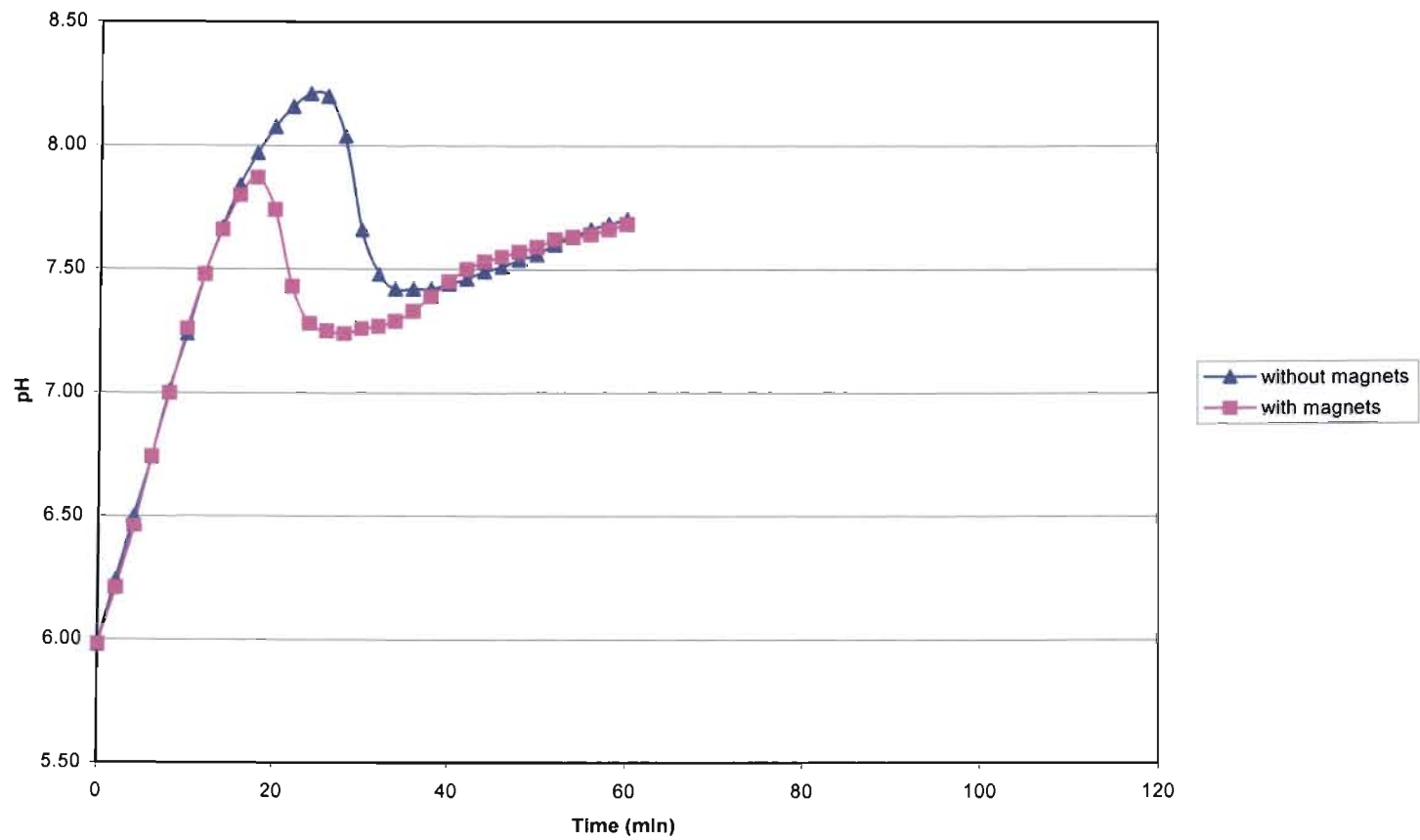
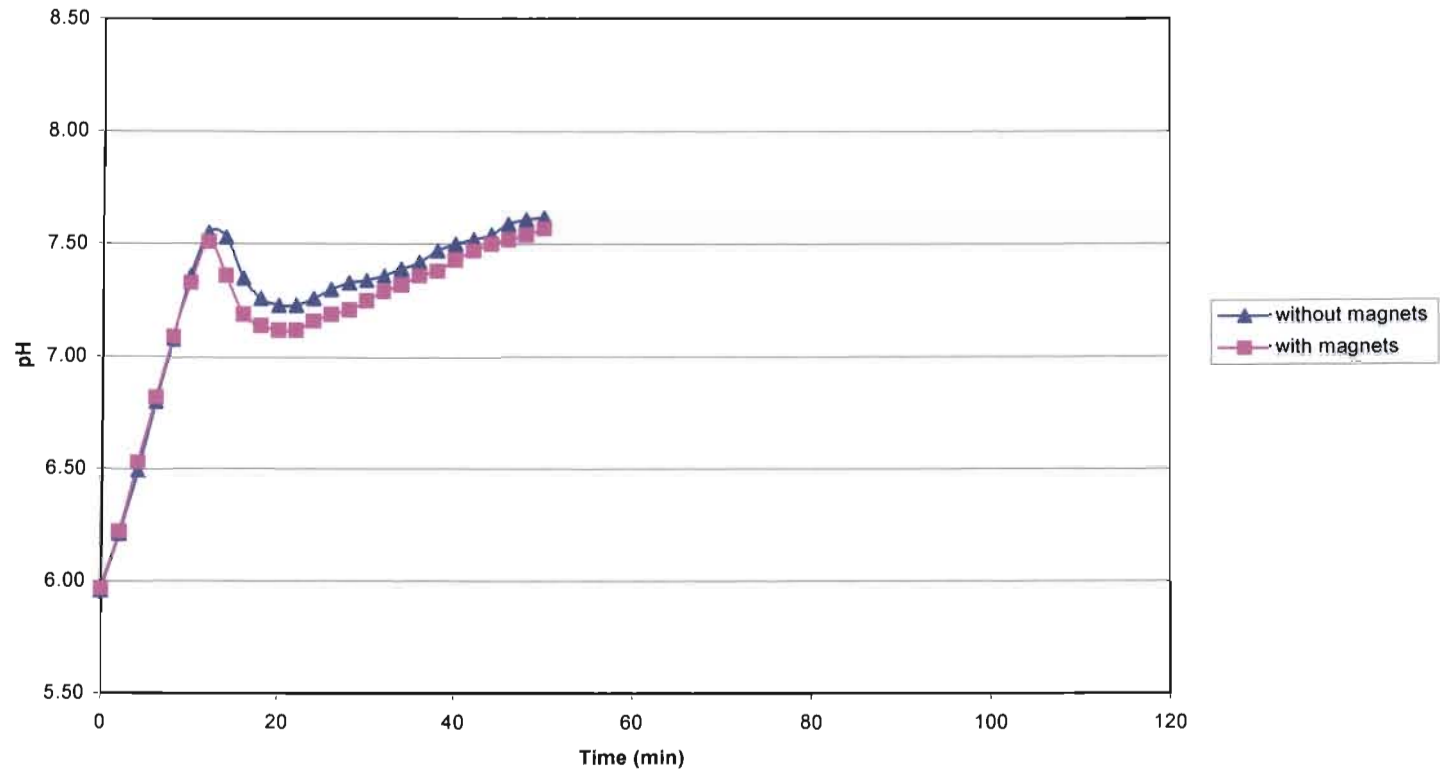


Fig. 4.5 – pH Graph for a Temperature of 50 °C



**Fig. 4.6 – pH Graph for a Temperature of 60 °C**



**Fig. 4.7 – pH Graph for a Temperature of 70 °C**

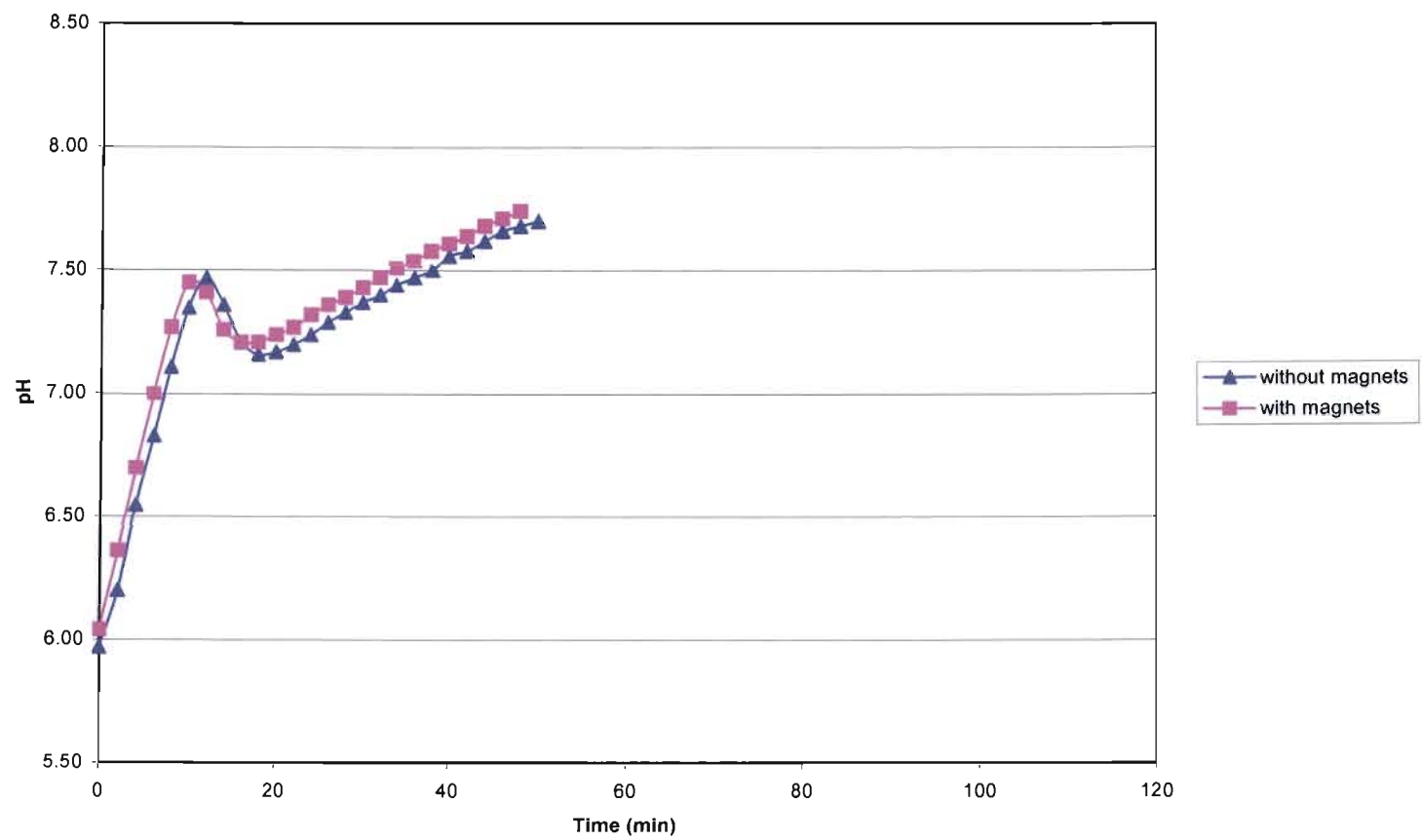


Fig. 4.8 – pH Graph for a Temperature of 80 °C

From the graphs (Figs. 4.3 to 4.8) it can be seen that as temperature increased, the time taken to reach the start of precipitation decreased. This was because the higher the temperature, the faster the release of carbon dioxide from the solution, which meant that the solution reached a supersaturated point faster.

The higher the temperature, the lower the pH at which precipitation started. When a solution is heated slowly it is possible to take the solution to a supersaturated state, however, if it is heated at a faster rate, the solution does not become supersaturated. As soon as it is saturated, precipitation starts. This feature is clearly demonstrated by the graphs.

The slope of the graphs gets steeper (during precipitation) as temperature is increased. This is because at higher temperatures the precipitation process was faster since carbon dioxide was being removed at a faster rate.

There was a greater difference between the two graphs (with and without the magnets) at lower temperatures. At high temperatures the graphs were almost overlapping, indicating that the precipitate that formed was the same in both the cases (with and without the magnets). This could also be seen from the X-ray diffraction analysis of the precipitate (Table 4.1). At low temperatures, the difference in the amounts of calcite and aragonite produced was greater than that at higher temperatures, since at higher temperatures, only aragonite was produced both, with and without the magnets.

The duration of the precipitation decreased as temperature was increased. Considering that the rate of precipitation increases with temperature, the actual precipitation process will be shorter as the mass of material available is constant. Once the solution reached an unsaturated state (quicker at higher temperatures since carbon dioxide is being driven off faster), it would not precipitate.

Table 4.1 and Fig. 4.9 show the results of X-ray diffraction analysis of the different proportions of calcite and aragonite at different temperatures.

Temperature	Without Magnets		With Magnets	
	% Aragonite	% Calcite	% Aragonite	% Calcite
30 °C	60	40	96	4
40 °C	67	33	92	8
50 °C	74	26	99	1
60 °C	90	10	98	2
70 °C	100	0	100	0
80 °C	100	0	100	0

Table 4.1 – Precipitate Composition at Different Temperatures

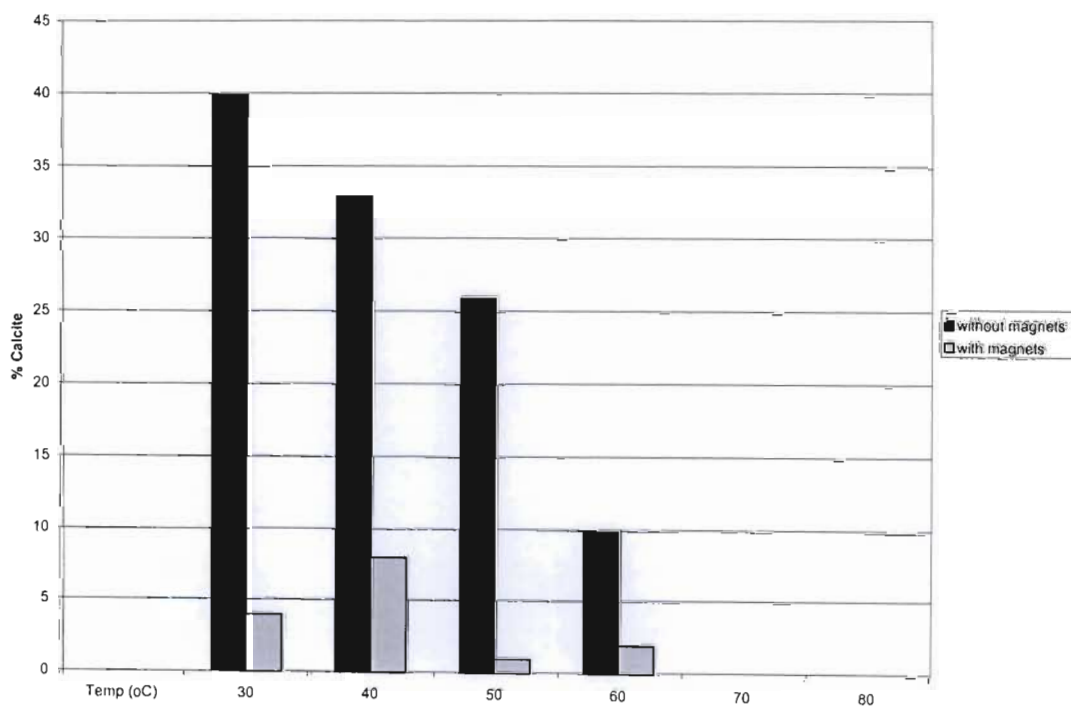


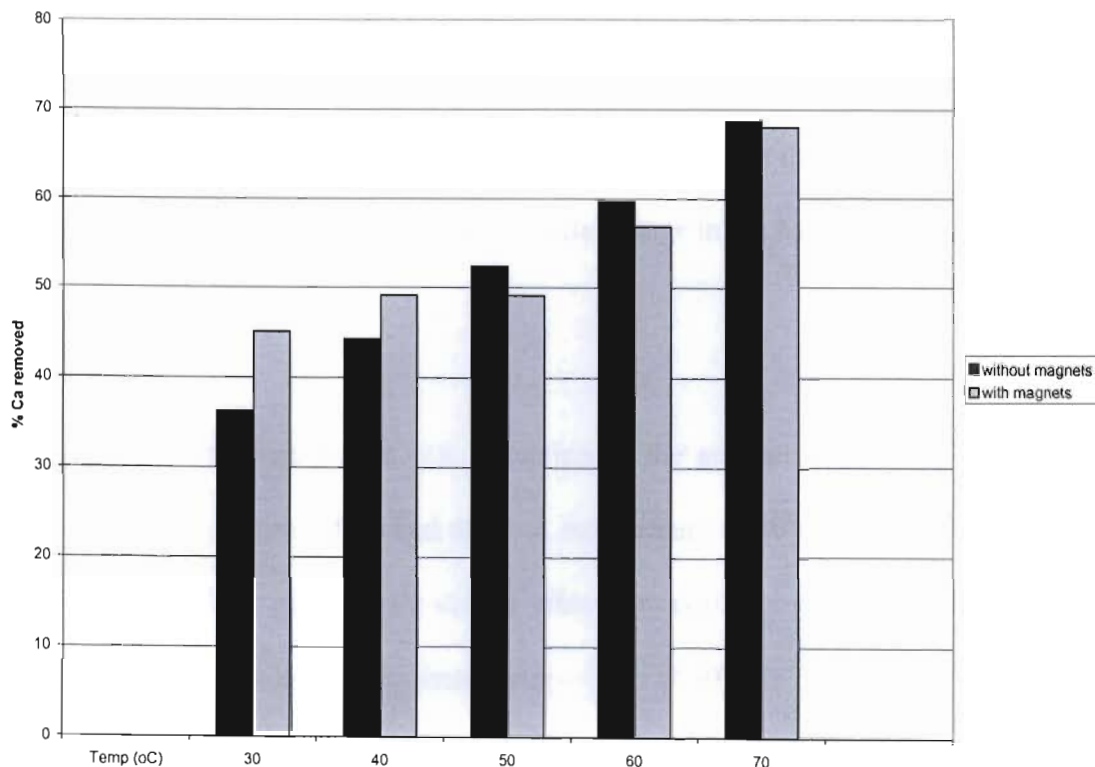
Fig. 4.9 – Precipitate Composition at Different Temperatures



Table 4.1 shows that the amount of calcite was reduced considerably by the use of the magnetic field. Once again, calcite is the main constituent of scale and this structure causes adhesion to the heating and piping surfaces. Aragonite is a much softer crystal, and as a result it does not adhere to any surface. It remains suspended in the solution and is carried to a place where there is a reduction of flow rate and the precipitate can settle out. Therefore, by reducing the amount of calcite present in any precipitate, there is a reduction in the amount of scale formed.

Another observation was that the amount of calcite present in the precipitate without the magnets decreased as temperature increased. This was due to the fact that at higher temperatures the carbon dioxide was driven off at a faster rate and as a result the precipitation was faster, favoring the aragonite structure. This may not happen under normal conditions, but was seen in these experiments because of the acceleration of the process. However, this could indicate that scale is only formed at low temperatures (during start up and shut down) and during normal steady operation only aragonite is formed. The calcite present in the system would cause all the calcium carbonate (calcite and aragonite) to form scale. Further investigations may be required to test if this is indeed the case. It can be seen from Figs. 4.7. and 4.8 that there is no difference in the two graphs (with and without the magnets) because pure aragonite occurs in both processes whether the magnets are used or not. Therefore the effect of temperature on the effectiveness of the magnetic field at high temperatures could not be evaluated.

Fig. 4.10 shows the percentage of calcium removed at different temperatures with and without the magnets.



**Fig. 4.10 – Effect of Temperature on Hardness of Filtrate**

The amount of calcium removed was calculated by subtracting the hardness of the filtrate from the hardness of the feed and was expressed as a percentage of the feed hardness. From the graph it can be clearly seen that the percentage calcium removed increased with temperature. The higher the temperature, the greater the amount of carbon dioxide removed from the solution and as a result, the greater the amount of precipitate formed. The effect without the magnets was seen to be linear between the above temperature

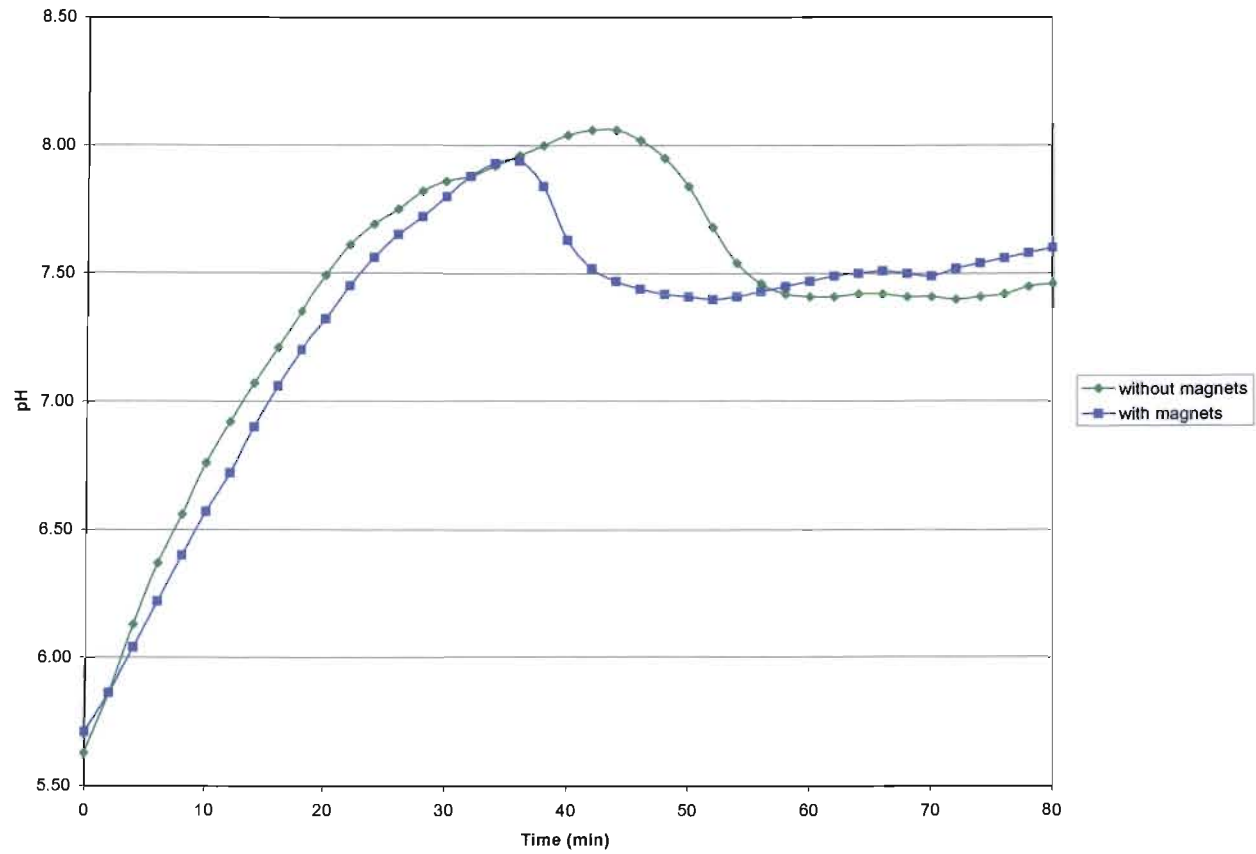
#### 4.4 Effect of Flow Rate

Literature stated that the magnetic treatment of water is successful only at flow rates in the laminar or transitional regimes. The effect of flow rate on the effectiveness of the treatment was tested.

The preferred method of preparing the feed (as stated by method 3 in Section 3.2.2) was used to prepare the feed at room temperature. Flow rates of 150, 200, 300 and 400 l/hr were investigated. Refer to Appendix A for the residence time calculations.

A feed of 3.5 litres of hard water was charged to the system and heated to 40°C. The flow control valve was opened to allow for the required flow rate. The solution was allowed to circulate through the system while maintaining a constant temperature and constant flow rate.

Figs. 4.11 to 4.14 show how pH changed with respect to time for systems, with and without the magnets at various flow rates.



**Fig. 4.11 – pH Graph for a Flow Rate of 150 l/hr (Re = 2083)**

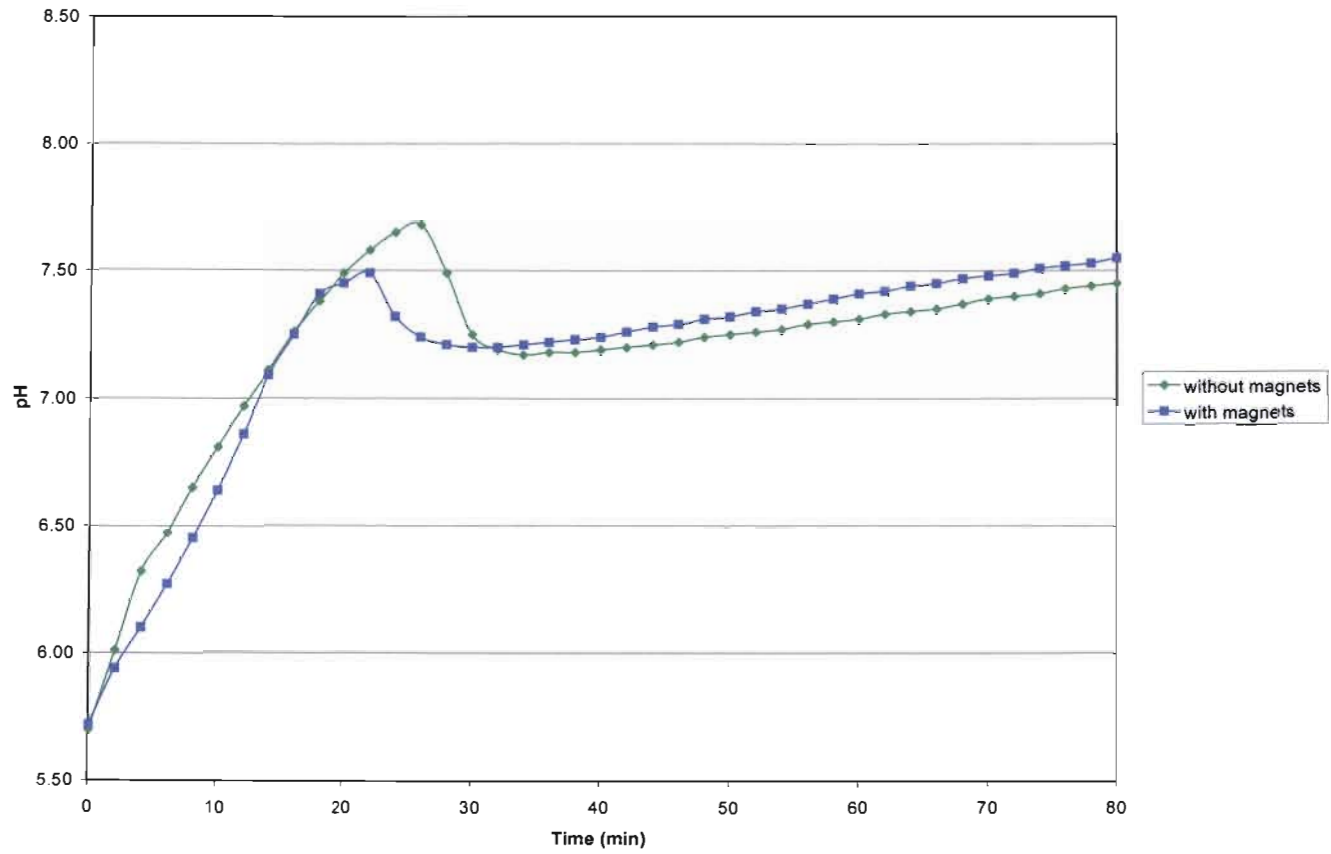


Fig. 4.12 – pH Graph for a Flow Rate of 200 l/hr (Re = 2777)

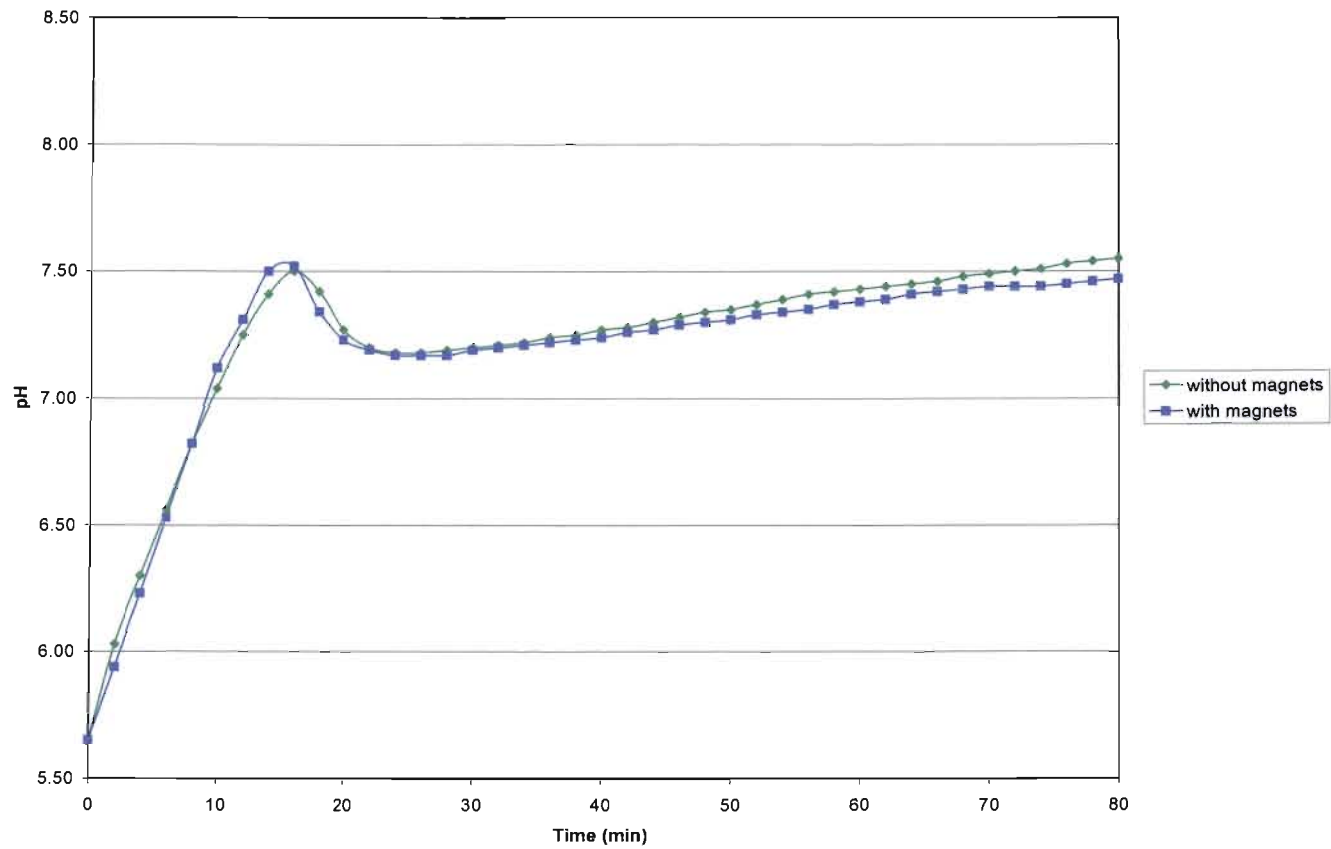
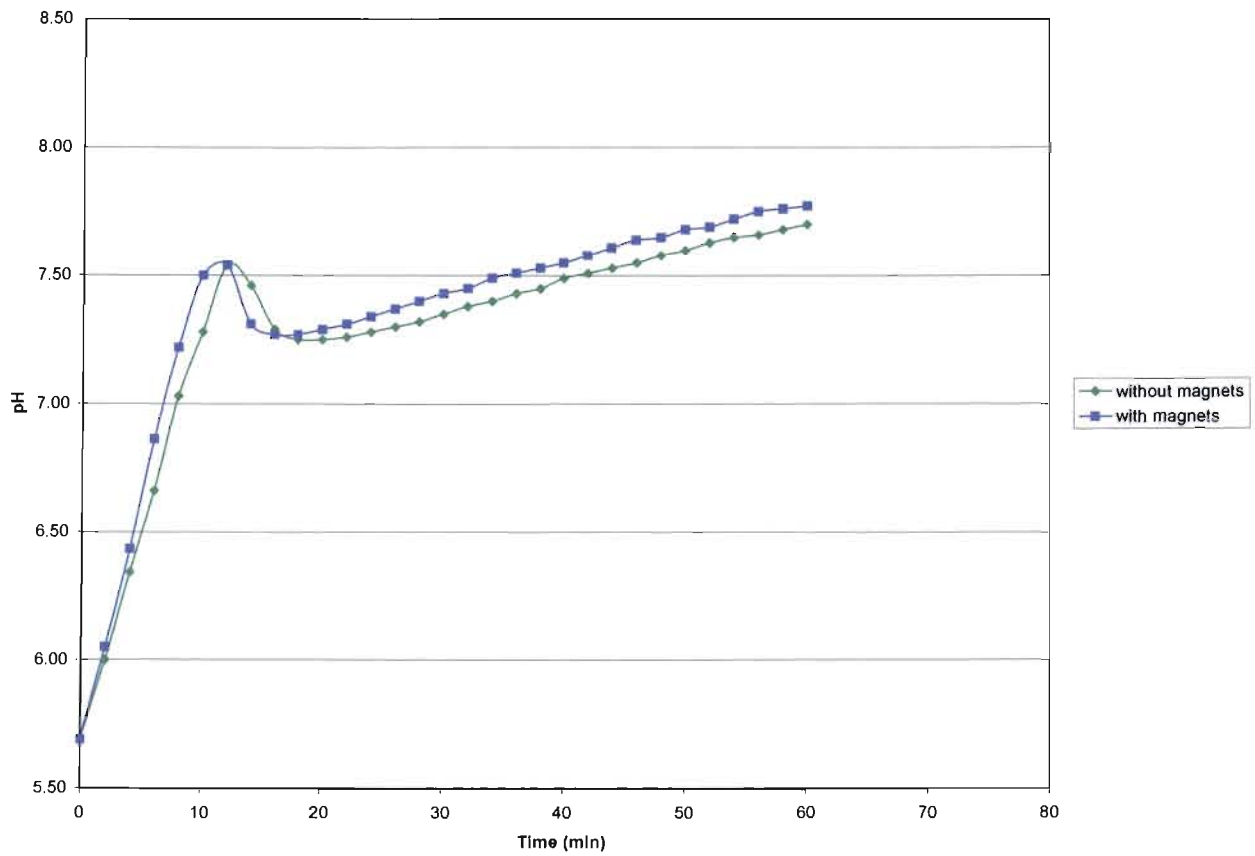


Fig. 4.13 – pH Graph for a Flow Rate of 300 l/hr (Re = 4166)



**Fig. 4.14 – pH Graph for a Flow Rate of 400 l/hr (Re = 5555)**

From the graphs (Figs. 4.11 to 4.14) it can be seen that there was a distinct difference between the curves (with and without magnets) at 150 and 200 l/hr. The other flow rates (300 and 400 l/hr) showed that curves were very similar and the difference was minimal. This was also confirmed from the X-ray diffraction analysis (Table 4.2).

When the flow rate was above 200 l/hr, the water was in the transitional flow regime. Eddies formed in the solution increased the collision of particles and thus also increased the rate at which carbon dioxide left the system. This increased the rate of precipitation and the faster rate favored the aragonite precipitate. This can also be seen from Table 4.2.

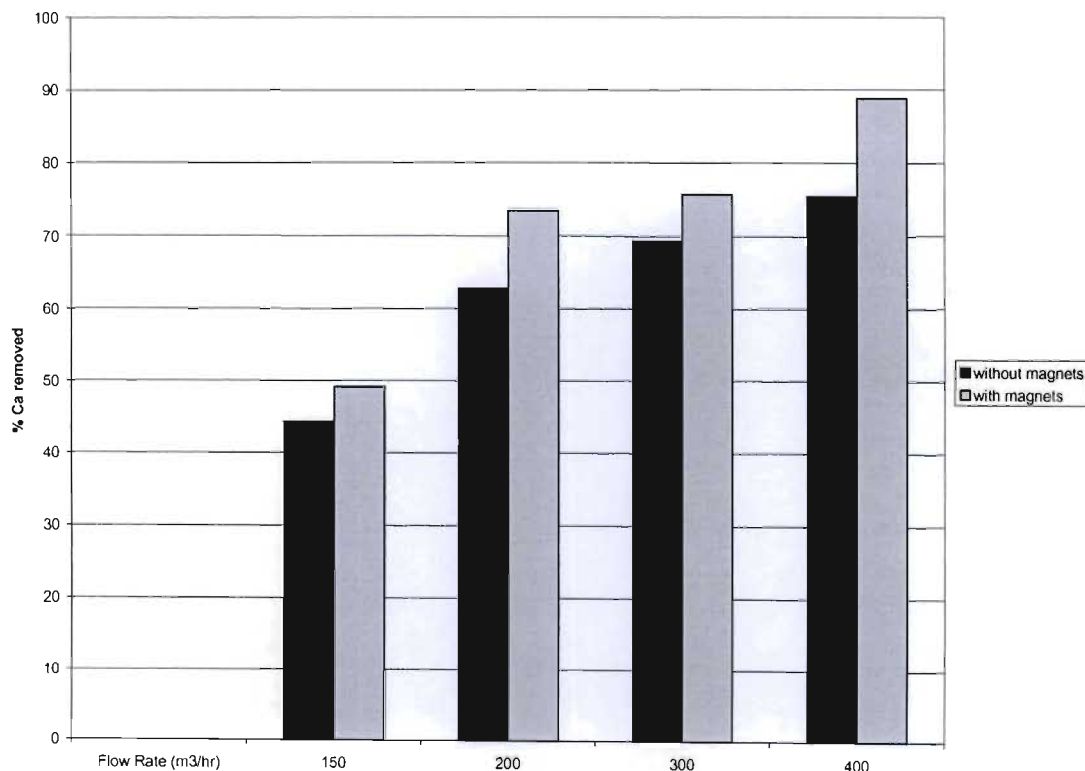
Since calcite could not be produced in the turbulent regime (due to the acceleration of the precipitation process), it was difficult to conclude the effect of flow rate on the effectiveness of magnetic water treatment.

Flow Rate	Without Magnets		With Magnets	
l/hr	% <i>Aragonite</i>	% <i>Calcite</i>	% <i>Aragonite</i>	% <i>Calcite</i>
150 (Re = 2083)	67	33	92	8
200 (Re = 2777)	99	1	99.2	0.8
300 (Re = 4166)	100	0	100	0
400 (Re = 5555)	100	0	100	0

**Table 4.2 – Precipitate Composition at Different Flow Rates**



There is a distinct difference, however, in the amount of calcium removed. The general trend is that the amount of calcium removed increased with flow rate (Fig. 4.15). As the flow rate increased, the amount of carbon dioxide leaving the system also increased (due to the vigorous mixing of the fluid in the turbulent regime) and as a result the greater the amount of precipitate formed, reducing the hardness of the water. With the magnetic field, the amount of calcium removed was greater at any particular flow rate. This meant that the magnetic field reduced the hardness of the water even when the water was flowing in the turbulent regime.



**Fig. 4.15 – Effect of Flow Rate on Hardness of Filtrate**

#### 4.5 Electron Microscope Observations

Figs. 4.16 and 4.17 indicate the structures of aragonite and calcite as would be seen under a Scanning Electron Microscope (SEM) [20,21]. Aragonite is a much softer crystal and under a high magnification appears to have spikes. This morphology reduces settling rates and prevents the crystal from adhering to piping and heat transfer surfaces.

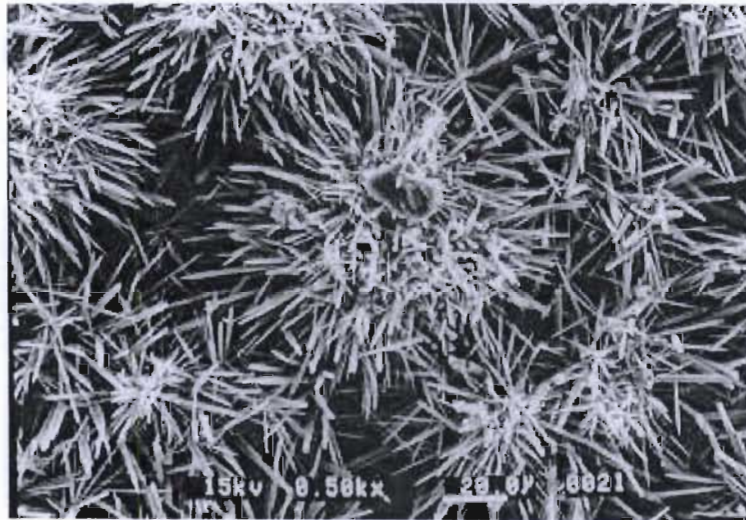


Fig. 4.16 – SEM Observation of Aragonite [20]

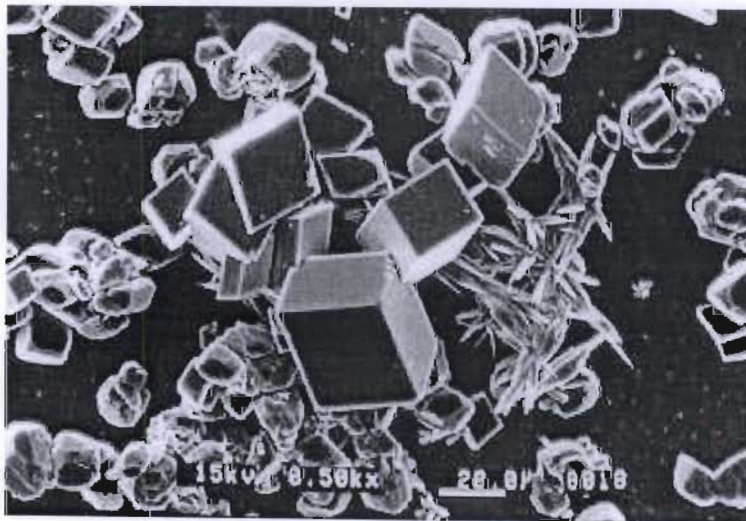
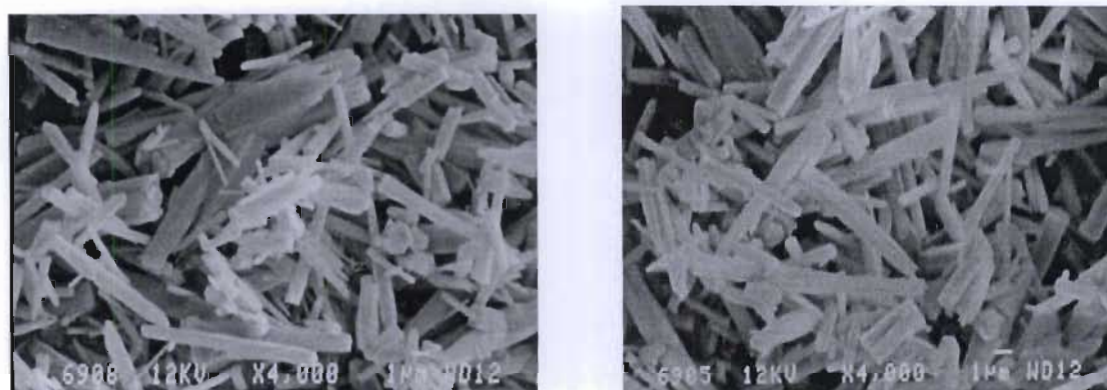
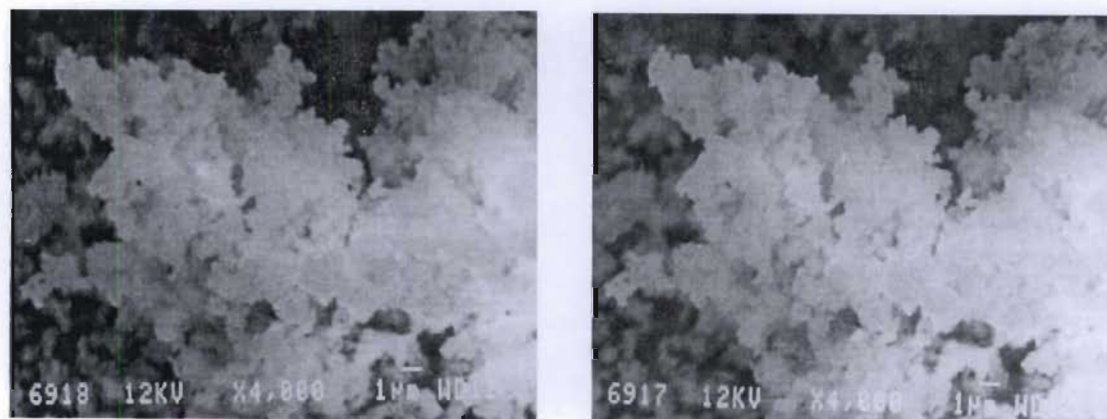


Fig. 4.17 – SEM Observation of Calcite [21]

Samples of precipitates were chosen from different experiments to observe under the Electron Microscope at a magnification of x4 000. X-ray diffraction showed that sample A (Fig. 4.18) was pure aragonite, while sample B (Fig. 4.19) was pure calcite and sample C (Fig. 4.20) was a combination of the two structures (40% calcite and 60% aragonite). Each figure below shows two separate photographs of each sample.

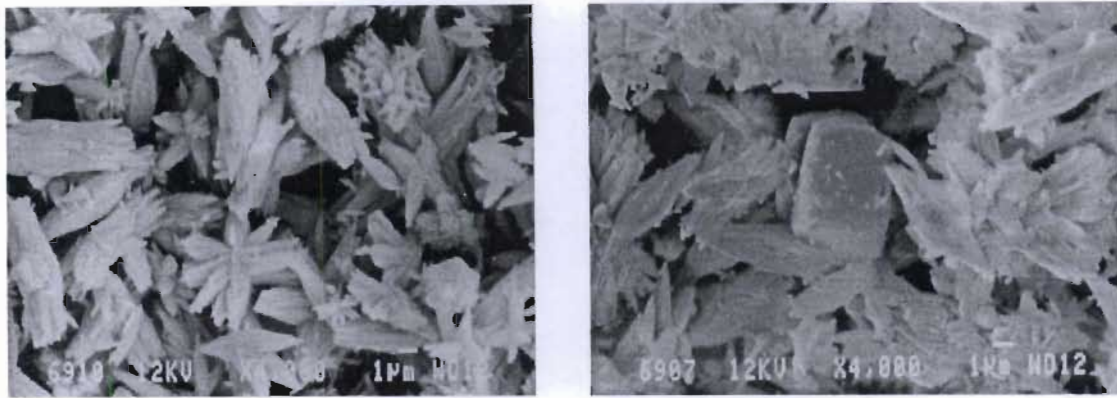


**Fig. 4.18 – SEM Photographs of Aragonite (Sample A)**



**Fig. 4.19 – SEM Photographs of Calcite (Sample B)**

The photographs (Figs. 4.18 and 4.19) were similar to those found in literature. Aragonite (Fig. 4.18) had a spike/needle-like crystal structure while calcite (Fig. 4.19) had a clustered appearance.



**Fig. 4.20 – SEM Photographs of Calcite and Aragonite Combination (Sample C)**

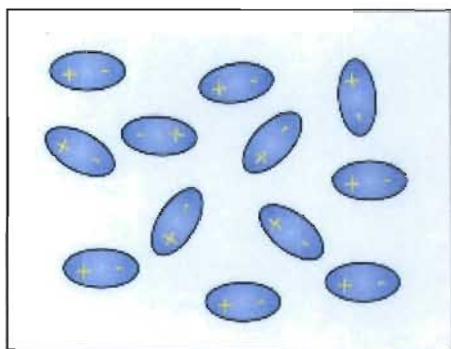
Both the needle-like structure of aragonite and rhombic structure of calcite were observed for sample C, which was a combination of the two minerals. The twinning effect of structures was evident forming star and flower-like crystal structures. This is the reason that the combined structures shown above would also adhere to piping and heat transfer surfaces.

#### **4.6 Possible Mechanism Behind Successful Application**

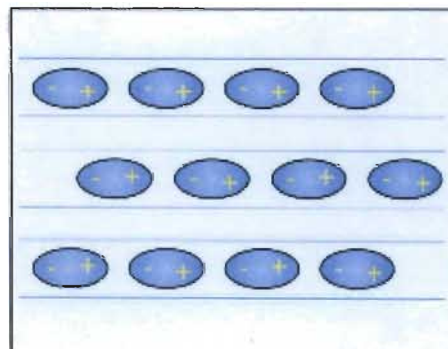
The dissolved ions ( $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ ) attract the dipolar water molecules around them and these water molecules (together with the dissolved carbon dioxide) form the Stern Layer around the ions. The ions therefore remain far apart from each other and do not come close enough to combine and form solid calcium carbonate.

Water molecules are dipolar. When these molecules flow they cause a flow of charge and as a result an electric current is created. The random dipolar molecules of the water (Fig. 4.21) orientate themselves in an ordered manner (Fig. 4.22) as they pass through the

magnetic field as a result of the Lorentz effect. The Stern Layer around the ions is then altered and the ions are brought closer together. The charged particles now form nucleation sites (homogeneously in the bulk of the solution as opposed to heterogeneously on any metal surfaces) for precipitation and this cause precipitation to occur faster than it would have if the molecules were just randomly arranged. If precipitation occurs at a faster rate, the aragonite structure is favored. As the nucleation sites form, the turbidity of the solution increases and high turbidity also favors aragonite being formed instead of calcite. Therefore aragonite continues to form in the solution.



**Fig. 4.21 – Random Arrangement  
of Water Molecules**



**Fig. 4.22 – Ordered Arrangement  
of Water Molecules**

This is in contradiction to most literature that stated that the effect of the magnetic field is to increase the solubility of calcium carbonate. This thesis shows that magnetisation increases the rate of precipitation and thus precipitates aragonite instead of calcite.

## CHAPTER 5

### CONCLUSION

Calcite and aragonite are both polymorphs of calcium carbonate. Scale is made up of essentially calcite, which is a hard, rhombic crystal and adheres to piping and heating surfaces. Aragonite is a much softer acicular crystal and does not adhere to surfaces. It precipitates out in the bulk of the solution and stays in suspension until it reaches a point where the velocity of the fluid is reduced to the extent that it can settle out.

By passing a saturated solution of calcium carbonate through a magnetic field, the water molecules align themselves to bring the dissolved ions closer together forming nucleation sites where precipitation can take place homogeneously. As a result the precipitation process is accelerated and the favoured crystal structure for an increased precipitation rate is aragonite. As crystals form in the solution, it increases the turbidity of the solution, and this also favours the formation of aragonite. In this way, the formation of scale (calcite) is reduced or stopped all together, since virtually 100% of aragonite is formed.

pH versus time graphs (Figs. 4.3 to 4.8 and 4.11 to 4.14) were used to observe the difference between the rates of precipitation with and without the magnets. It was observed that the precipitation process for the system with the magnets generally started before that for systems without the magnets. This is in contradiction to the literature surveyed, which stated that the magnetic field increased the solubility of the calcium carbonate. Experiments conducted in this thesis confirmed that magnetization increased

the rate of precipitation of calcium carbonate and thus favored the aragonite crystal structure.

The composition of the precipitate was tested with X-ray diffraction and was also observed under the electron microscope to observe the different structures.

The effect of increasing temperature of the solution increased the rate of precipitation, once again favouring the aragonite crystal structure. The magnetic system worked efficiently in the laminar/transitional regimes, but the effect could not be tested in the turbulent regime, since pure aragonite was being formed even without the magnets (due to the acceleration of the precipitation process). Atomic absorption was used to find the hardness of the feed and filtrate samples. It was found that the amount of calcium removed increased with temperature and flow rate.

It is a well-known fact that scale is a cause of corrosion (although it is not the only cause). By reducing the amount of scale, the extent of corrosion is also reduced. Another benefit is that the concentration of corrosion control chemicals will also be reduced.

For future research, it is recommended that the system be upgraded from bench-top to a pilot scale. The feed may now be prepared at a lower hardness in order to decrease the precipitation rate. The system should be set up so that the precipitation takes approximately a week to occur. The piping network should be increased so as to accommodate a greater capacity of solution and allow for evaporation of the water.

Online pH and turbidity meters should be attached to a data logger to take measurements at constant time intervals.

Using this setup, the precipitation will not be as fast as reported in this thesis and more calcite could be formed without the magnets to try and simulate the real situation better. More conclusive results would be obtained from these experiments.

Other magnets may also be tested and compared such as ceramic magnets and electromagnets. The effect of magnetic field strength could also be tested in order to obtain the optimum strength. An electric wire could be wrapped around the pipe as a coil to test if the magnetic field generated by this electromagnet would be sufficient to cause any change in the precipitation process.

It is stated in literature that aragonite would eventually convert to calcite. The time taken for this to occur needs to be investigated. The memory of the magnetic treatment should also be looked at to see how far downstream the magnetically treated water is still effective in the prevention of scale.



It is reported in literature that existing scale is removed from piping and heat transfer surfaces by passing magnetically treated water through it. It is assumed that the magnetic field would change the crystal structure of calcite to aragonite so that it is carried in suspension through the system. Tests will have to be done to confirm this. The experimental system would have to run without the magnets to produce calcite. The magnets would then be attached and the precipitate obtained after a specified time period would be tested using X-ray diffraction and electron microscope observations to test if any change in composition occurs.

## NOMENCLATURE

$G'$	amount of scale build up ( $\text{g}/\text{m}^3$ )
$q'$	heat load of a heat exchanger ( $\text{kW}/\text{m}^2$ )
$\bar{q}'$	dimensionless heat load ( $\bar{q}' = q' / q'_r$ , $q'_r = 1 \text{ kW}/\text{m}^2$ )
$\tau$	dimensionless time ( $\tau = \tau / \tau_r$ , $\tau_r = 1$ hour)
$\eta$	coefficient of reduction of deposits
$\mu_0$	permeability of free space ( $4\pi \times 10^{-7} \text{ T}\cdot\text{m}/\text{A}$ )
$B$	magnetic flux (tesla)
$F$	force (N)
$G$	amount of scale formed (mg)
$H$	externally applied magnetic force (A/m)
$K_e$	equilibrium factor
$K_{sp}$	solubility product constant
$M$	magnetisation (A/m)
$q$	charge of a particle (C)
$Sr$	supersaturation ratio
$t$	time (s, hr)
$v$	velocity (m/s)

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## APPENDIX A

### Calculations

#### *Calculation of Feed Capacity*

The total volume of the piping system (without the feed tank) was calculated as follows:

Material	Diameter (mm)	x-sect. Area (m <sup>2</sup> )	Length (m)	Volume (m <sup>3</sup> )	Volume (litres)
silicone tube	9	0.000063617	2.3	0.0001463	0.15
glass	25.4	0.000506707	2.15	0.0010894	1.09
policorp	19	0.000283529	2.7	0.0007655	0.77
Total				0.0020013	2.01

Therefore the fluid in the piping network occupied a volume of two litres. As a result the maximum allowable feed that could be used (to ensure that all the fluid passes through the magnetic field) was 4 litres. A volume of 3.5 litres was chosen for the feed.



### ***Calculation of Residence Time***

To investigate the effect of temperature on magnetic water treatment, a constant flow of 150 l/hr was used for all the temperatures. Since the volume of fluid in the pipe work was 2 litres, the time taken for the fluid to move through the system was:

$$\text{Time for 150 l/hr} = \frac{2l}{150l/hr} = 0.0133hr = 48 \text{ seconds}$$

Similarly,

Flow rate (l/hr)	Residence Time (s)
200	36
300	24
400	18

### ***Calculation of Hardness for Feed Preparation***

In order to prepare the feed using method 3, 2g of  $\text{CaCO}_3$  was added to 4 litres of distilled water.

$$\text{Number of moles of } \text{CaCO}_3 = \text{mass} / \text{molar mass}$$

$$= \frac{2}{100}$$

$$= 0.02 \text{ mol}$$

$$\text{Number of moles } \text{Ca}^{2+} = 0.02 \text{ mol}$$

$$\text{Therefore mass } \text{Ca}^{2+} = \text{no. of moles} \times \text{molar mass}$$

$$= 0.02 \times 40$$

$$= 0.8 \text{ g}$$

$$\begin{aligned} \text{Therefore hardness} &= \frac{800 \text{ mg}}{4 \text{ l}} \\ &= 200 \text{ ppm} \end{aligned}$$

The feed was prepared so that it would have a hardness of approximately 200 ppm.

### ***Calculation of Volumetric Flow Rate***

The flow of water in the system should be laminar or in the transitional mode for magnetic treatment to be effective. Therefore, the volumetric flow rate had to be chosen so as to have a Reynolds number < 2300 (which is the critical value for flow in a pipe). A flow rate of 150 l/hr was chosen and the Reynolds number is calculated below:

$$\begin{aligned} \text{Physical properties of water: density} &= 1000 \text{ kg/m}^3 \\ \text{Viscosity} &= 0.001 \text{ Pa.s} \end{aligned}$$

$$\begin{aligned} \text{X-sectional area of glass tube (25.4 mm diameter)} &= \frac{\pi d^2}{4} \\ &= \frac{\pi (0.0254)^2}{4} \\ A &= 5.067 \times 10^{-4} \text{ m}^2 \\ \text{Volumetric flow rate (Q) = 150 l/hr} &= 4.167 \times 10^{-5} \text{ m}^3/\text{s} \\ \text{Velocity in glass tube} &= Q/A \\ &= \frac{4.167 \times 10^{-5}}{5.067 \times 10^{-4}} \\ &= 0.082 \text{ m/s} \end{aligned}$$

Therefore Reynolds number

$$\begin{aligned} &= \frac{\rho u d}{\mu} \\ &= \frac{(1000)(0.082)(0.0254)}{0.001} \\ &= 2083 \end{aligned}$$

Since this value is below 2300 it is acceptable for laminar flow.

Similarly:

Volumetric Flowrate (l/hr)	Velocity (m/s)	Reynolds Number
200	0.110	2777
300	0.164	4166
400	0.219	5555

## **APPENDIX B**

### **Results Obtained Using Feed Preparation by Method 2**

Table AB1 shows some of the absorbance and pH results obtained when the runs were conducted with a feed that was prepared by method 2.

time (min)	w/o		w		w		w/o		w/o	
	pH	Abs	pH	Abs	pH	Abs	pH	Abs	pH	Abs
0	7.28	0.000	7.24	0.000	7.32	0.000	7.38	0.000	7.43	0.000
1										
2	7.31	0.000	7.30	0.002	7.40	0.000	7.44	0.000	7.55	0.000
3			7.32	0.002	7.45	0.000	7.47	0.000	7.58	0.000
4	7.39	0.000	7.33	0.006	7.48	0.000	7.50	0.000	7.59	0.000
5	7.42	0.000	7.32	0.006	7.51	0.000	7.53	0.000	7.61	0.000
6			7.31	0.008	7.53	0.000	7.54	0.000	7.62	0.000
7	7.49	0.000	7.29	0.011	7.55	0.000	7.57	0.000	7.62	0.000
8			7.26	0.015	7.57	0.000	7.58	0.001	7.62	0.000
9	7.53	0.000	7.23	0.021	7.59	0.000	7.58	0.001	7.61	0.000
10			7.20	0.028	7.61	0.000	7.59	0.002	7.60	0.000
11	7.53	0.000	7.16	0.035			7.61	0.004	7.59	0.000
12			7.12	0.046	7.63	0.000	7.63	0.005		0.000
13	7.51	0.000	7.08	0.062	7.63	0.000	7.64	0.009	7.55	0.000
14			7.06	0.072	7.63	0.000	7.64	0.011	7.54	0.000
15	7.48	0.000	7.02	0.089	7.64	0.000	7.64	0.017	7.54	0.000
16			6.99	0.106	7.64	0.000	7.64	0.027	7.54	0.000
17	7.42	0.007	6.96	0.126	7.64	0.000	7.63	0.041	7.53	0.000
18	7.40	0.012	6.93	0.149	7.65	0.000	7.61	0.060	7.53	0.000
19	7.37	0.018	6.91	0.167	7.64	0.000	7.58	0.081	7.52	0.000
20	7.35	0.023	6.89	0.189	7.64	0.000	7.54	0.107	7.51	0.000
21	7.32	0.028	6.87	0.208	7.63	0.000	7.50	0.131	7.49	0.000
22	7.30	0.035	6.86	0.229	7.62	0.000	7.46	0.158	7.46	0.007
23	7.28	0.073	6.84	0.251	7.60	0.000	7.42	0.182	7.44	0.012
24	7.27	0.048	6.82	0.268			7.39	0.203	7.40	0.028
25	7.24	0.057	6.81	0.289	7.55	0.000	7.35	0.223	7.37	0.041
26	7.23	0.057	6.80	0.309	7.50	0.004	7.32	0.242	7.34	0.058

27	7.22	0.062	6.79	0.332	7.44	0.029	7.32	0.258	7.33	0.075
28	7.21	0.068	6.78	0.348	7.38	0.055	7.31	0.274	7.31	0.091
29	7.20	0.075	6.74	0.367	7.33	0.072	7.29	0.286		
30	7.19	0.082	6.73	0.389	7.29	0.094	7.28	0.300	7.29	0.127
31	7.18	0.089	6.70	0.409	7.25	0.115	7.27	0.312	7.28	0.141
32	7.17	0.095	6.69	0.426	7.22	0.134	7.26	0.324	7.28	0.157
33	7.16	0.104	6.68	0.444	7.20	0.153	7.26	0.333	7.29	0.173
34	7.15	0.109	6.67	0.461	7.18	0.170	7.26	0.343	7.27	0.186
35	7.13	0.124	6.66	0.477	7.16	0.186	7.25	0.356	7.27	0.201
36	7.14	0.130	6.66	0.493	7.14	0.203	7.24	0.367	7.27	0.212
37	7.13	0.132	6.66	0.520	7.13	0.219	7.23	0.377	7.27	0.225
38	7.13	0.146	6.66	0.528	7.14	0.236	7.22	0.388	7.27	0.240
39	7.12	0.146	6.65	0.545	7.13	0.252	7.22	0.400	7.26	0.252
40	7.12	0.153	6.65	0.561	7.12	0.270	7.21	0.411	7.26	0.263
41	7.12	0.161	6.64	0.580	7.10	0.287	7.21	0.421	7.26	0.276
42	7.11	0.166	6.64	0.593	7.09	0.301	7.20	0.433	7.25	0.286
43	7.11	0.174	6.63	0.609	7.07	0.318	7.20	0.445	7.25	0.300
44	7.11	0.181	6.63	0.626	7.06	0.333	7.20	0.458	7.24	0.312
45	7.11	0.187	6.63	0.645	7.05	0.348	7.20	0.568	7.24	0.323
46	7.12	0.194	6.63	0.660	7.04	0.365	7.21	0.480	7.24	0.333
47	7.12	0.199	6.62	0.688	7.02	0.379	7.20	0.492	7.24	0.345
48	7.12	0.206	6.62	0.693	7.02	0.392	7.20	0.503	7.25	0.357
49	7.12	0.212	6.61	0.710	7.00	0.408	7.19	0.515	7.26	0.370
50	7.12	0.224	6.62	0.726	6.99	0.422	7.19	0.527	7.28	0.380
51	7.13	0.229	6.61	0.744	6.98	0.438	7.19	0.541	7.30	0.390
52	7.13	0.235	6.61	0.761	6.96	0.453	7.20	0.553	7.31	0.399
53	7.13	0.242	6.61	0.775	6.94	0.468	7.19	0.565	7.32	0.408
54	7.14	0.255	6.61	0.794	6.93	0.481	7.19		7.32	0.420
55	7.15	0.261	6.61	0.806	6.92	0.497	7.19		7.33	0.433
56	7.15	0.267	6.60	0.821	6.92	0.514	7.19			

57	7.15	0.275	6.60	0.837	6.92	0.527	7.20	0.610	7.32	0.457
58	7.16	0.281			6.91	0.541	7.19	0.620	7.32	0.467
59	7.16	0.290	6.60		6.90	0.557	7.19	0.630	7.31	0.481
60	7.16	0.299			6.89	0.573	7.20	0.641	7.31	0.493
61	7.17	0.307	6.59		6.87	0.586	7.19	0.652	7.30	0.506
62	7.17	0.314			6.87	0.600	7.19	0.662	7.29	0.519
63	7.18	0.322	6.58		6.86	0.615	7.19	0.672	7.28	0.531
64	7.19	0.328			6.87	0.630	7.19	0.684	7.27	0.544
65	7.19	0.338	6.58		6.87	0.641	7.20	0.693	7.27	0.556
66	7.20	0.343			6.88	0.655	7.20	0.705	7.26	0.570
67	7.20	0.351			6.88	0.668	7.20	0.717	7.25	0.583
68	7.20	0.360			6.87	0.681	7.20	0.728	7.24	0.596
69	7.21	0.368			6.88	0.692	7.21	0.740	7.23	0.608
70	7.21	0.377	6.58		6.87	0.705	7.22	0.750	7.22	0.619
71	7.21	0.385			6.87	0.718	7.21	0.760	7.22	0.630
72	7.22	0.392			6.87	0.730	7.21	0.770	7.22	0.639
73	7.23	0.401			6.86	0.743	7.21	0.782	7.21	0.651
74	7.24	0.410			6.87	0.757	7.19	0.793	7.20	0.654
75	7.24	0.417			6.86	0.770	7.18	0.806	7.20	0.663
76	7.24	0.425			6.85	0.783	7.17	0.816	7.21	0.673
77	7.25	0.433			6.84	0.794	7.17	0.825	7.21	0.684
78	7.25	0.445			6.85	0.808	7.15	0.835	7.23	0.694
79			6.56		6.85	0.822	7.15	0.845	7.24	0.704
80	7.25	0.458			6.85	0.834	7.14	0.855	7.25	0.714
81	7.25	0.467			6.85	0.848	7.12	0.866	7.26	0.722
82	7.26	0.477			6.84	0.861	7.10	0.876	7.27	0.732
83	7.26	0.484			6.84	0.872	7.10	0.885	7.27	0.741
84	7.26	0.494			6.84	0.894	7.10	0.896	7.26	0.750
85	7.27	0.501			6.83	0.897	7.10	0.905	7.26	0.758
86	7.27	0.503			6.82	0.908	7.10	0.915	7.26	0.766

87	7.27	0.512			6.82	0.921	7.10	0.925	7.24	0.775
88	7.28	0.521			6.81	0.934	7.10	0.934	7.24	0.784
89	7.28	0.529			6.80	0.944	7.09	0.944	7.24	0.791
90	7.28	0.539			6.79	0.956	7.09	0.954	7.23	0.797
91	7.29	0.544			6.79	0.967	7.09	0.964	7.23	0.805
92	7.29	0.553	6.52		6.78	0.978	7.09	0.973	7.22	0.813
93	7.29	0.560			6.78	0.989	7.07	0.983	7.22	0.820
94	7.29	0.568								
95	7.29	0.575								
96	7.30	0.583								
97	7.31	0.592								
98	7.31	0.599			6.77	1.053	7.06	1.031	7.19	0.864
99	7.31	0.609								
100	7.31	0.614								
101	7.32	0.621								
102	7.33	0.630								
103	7.33	0.635					7.05	1.078	7.26	0.901
104	7.34	0.642								
105	7.34	0.650								
106										
107	7.35	0.666								
108										
109	7.36	0.678								
110									7.23	0.946
111	7.37	0.695			6.79	1.192				
112			6.59							
113	7.37	0.706								
114										
115	7.38	0.720	6.61							
116							6.98	1.192		



117	7.38	0.733								
118									7.20	0.995
119	7.38	0.746								
120			6.64		6.74	1.314	7.03	1.222		
121	7.39	0.764								
122										
123							7.06	1.240	7.27	1.018
124										
125										
126										
127										
128							7.03	1.272		

**Table AB1 - pH and Absorbance Results Obtained with Feed Preparation by Method 2**

w = experiments with magnets

w/o = experiments without magnets

## **APPENDIX C**

### **pH Data Results**

The raw data obtained for the pH measurements are tabulated below. Table AC1 shows the pH measurements at different temperatures for experiments with and without the magnets, while Table AC2 shows the results at different flow rates.



66	8.03	7.52	7.42	7.51									
68	7.96	7.50	7.41	7.50									
70	7.86	7.50	7.41	7.49									
72	7.76	7.50	7.40	7.52									
74	7.68	7.50	7.41	7.54									
76	7.64	7.51	7.42	7.56									
78	7.62	7.52	7.45	7.58		7.46							
80	7.61	7.53	7.46	7.60									
82	7.61	7.53	7.48	7.61									
84	7.61	7.55		7.63									
86	7.62	7.56	7.53	7.63									
88	7.63	7.57	7.53	7.63									
90	7.63	7.58		7.63									
92	7.63	7.60	7.50	7.63									
94	7.60	7.62	7.51	7.67									
96	7.58	7.63	7.54	7.70									
98	7.58	7.64	7.59										
100	7.58	7.65	7.60	7.73									
102	7.58	7.67		7.74									
104	7.59	7.68	7.64	7.75									
106	7.61	7.69	7.65	7.76									
108	7.62	7.70	7.65										
110	7.64	7.72	7.64										
112	7.66	7.73		7.75		7.59							
114	7.67	7.74											
116	7.69	7.74											
118	7.71	7.75											
120	7.72	7.76											

**Table AC1 - pH Data for Temperature Changes**

pH-w/o = pH measurements without magnets

pH-w = pH measurements with magnets

Time (min)	150 l/hr		200 l/hr		300 l/hr		400 l/hr	
	pH-w/o	pH-w	pH-w/o	pH-w	pH-w/o	pH-w	pH-w/o	pH-w
0	5.63	5.71	5.70	5.72	5.65	5.65	5.69	5.69
2	5.86	5.86	6.01	5.94	6.03	5.94	6.00	6.05
4	6.13	6.04	6.32	6.10	6.30	6.23	6.34	6.43
6	6.37	6.22	6.47	6.27	6.56	6.53	6.66	6.86
8	6.56	6.40	6.65	6.45	6.82	6.82	7.03	7.22
10	6.76	6.57	6.81	6.64	7.04	7.12	7.28	7.50
12	6.92	6.72	6.97	6.86	7.25	7.31	7.54	7.54
14	7.07	6.90	7.11	7.09	7.41	7.50	7.46	7.31
16	7.21	7.06	7.26	7.25	7.50	7.52	7.29	7.27
18	7.35	7.20	7.38	7.41	7.42	7.34	7.25	7.27
20	7.49	7.32	7.49	7.45	7.27	7.23	7.25	7.29
22	7.61	7.45	7.58	7.49	7.20	7.19	7.26	7.31
24	7.69	7.56	7.65	7.32	7.18	7.17	7.28	7.34
26	7.75	7.65	7.68	7.24	7.18	7.17	7.30	7.37
28	7.82	7.72	7.49	7.21	7.19	7.17	7.32	7.40
30	7.86	7.80	7.25	7.20	7.20	7.19	7.35	7.43
32	7.88	7.88	7.19	7.20	7.21	7.20	7.38	7.45
34	7.92	7.93	7.17	7.21	7.22	7.21	7.40	7.49
36	7.96	7.94	7.18	7.22	7.24	7.22	7.43	7.51
38	8.00	7.84	7.18	7.23	7.25	7.23	7.45	7.53
40	8.04	7.63	7.19	7.24	7.27	7.24	7.49	7.55
42	8.06	7.52	7.20	7.26	7.28	7.26	7.51	7.58
44	8.06	7.47	7.21	7.28	7.30	7.27	7.53	7.61
46	8.02	7.44	7.22	7.29	7.32	7.29	7.55	7.64
48	7.95	7.42	7.24	7.31	7.34	7.30	7.58	7.65
50	7.84	7.41	7.25	7.32	7.35	7.31	7.60	7.68
52	7.68	7.40	7.26	7.34	7.37	7.33	7.63	7.69
54	7.54	7.41	7.27	7.35	7.39	7.34	7.65	7.72
56	7.46	7.43	7.29	7.37	7.41	7.35	7.66	7.75
58	7.42	7.45	7.30	7.39	7.42	7.37	7.68	7.76
60	7.41	7.47	7.31	7.41	7.43	7.38	7.70	7.77
62	7.41	7.49	7.33	7.42	7.44	7.39		
64	7.42	7.50	7.34	7.44	7.45	7.41		
66	7.42	7.51	7.35	7.45	7.46	7.42		
68	7.41	7.50	7.37	7.47	7.48	7.43		
70	7.41	7.49	7.39	7.48	7.49	7.44		
72	7.40	7.52	7.40	7.49	7.50	7.44		
74	7.41	7.54	7.41	7.51	7.51	7.44		
76	7.42	7.56	7.43	7.52	7.53	7.45		
78	7.45	7.58	7.44	7.53	7.54	7.46		
80	7.46	7.60	7.45	7.55	7.55	7.47		

**Table AC2 - pH Data for Flow Rate Changes**

pH-w/o = pH measurements without magnets

pH-w = pH measurements with magnets

## **APPENDIX D**

### **Correlation of pH and Absorbance Graphs**

Fig AD1 shows further confirmation of the correlation between the absorbance and pH measurements.

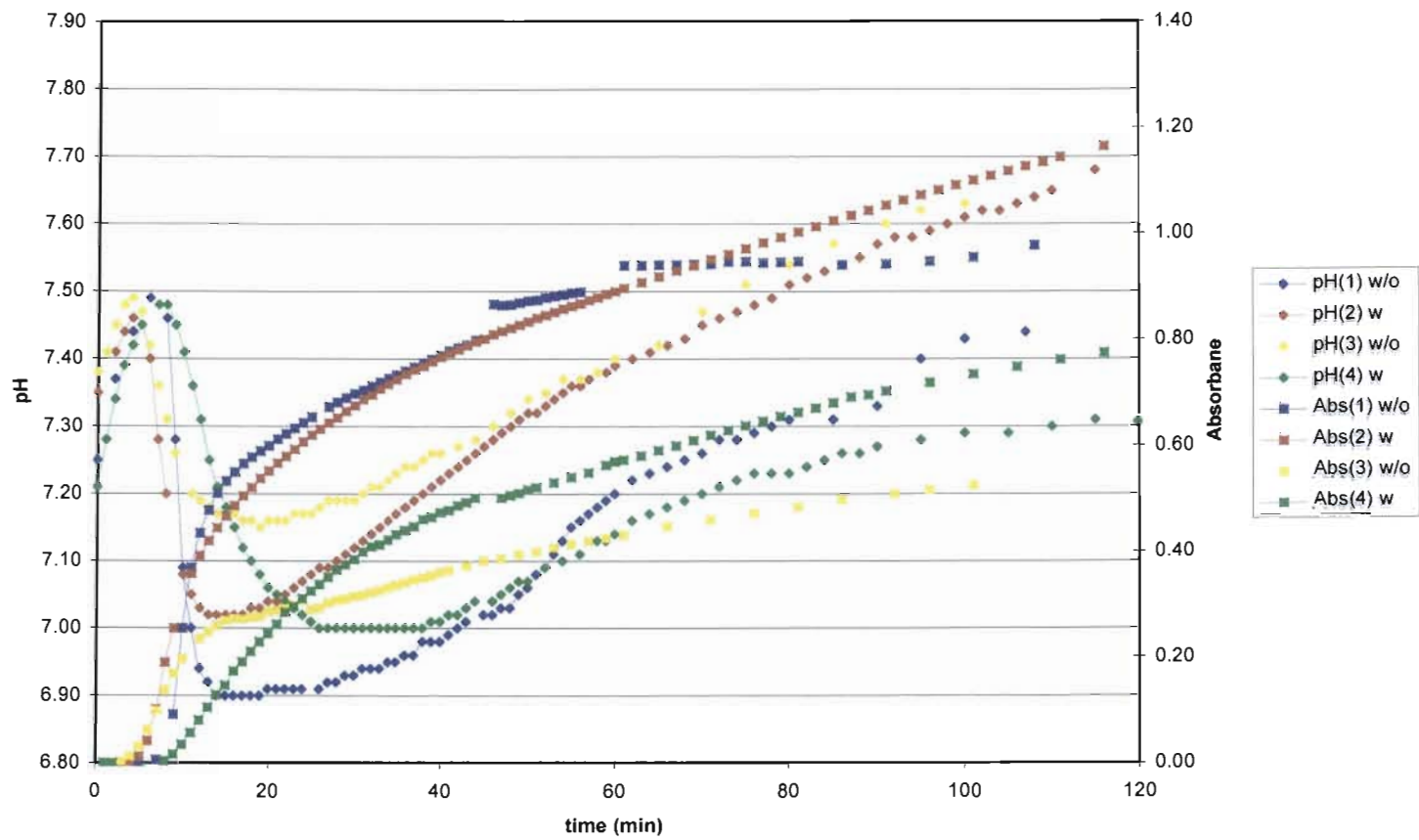


Fig. AD1 – Graph Showing the Correlation Between pH and Absorbance

## APPENDIX E

### X-Ray Diffraction Analysis

X-ray diffraction was used to identify the composition of the precipitates. Figs. AE1 and AE2 show typical results obtained from the X-ray diffraction analysis.

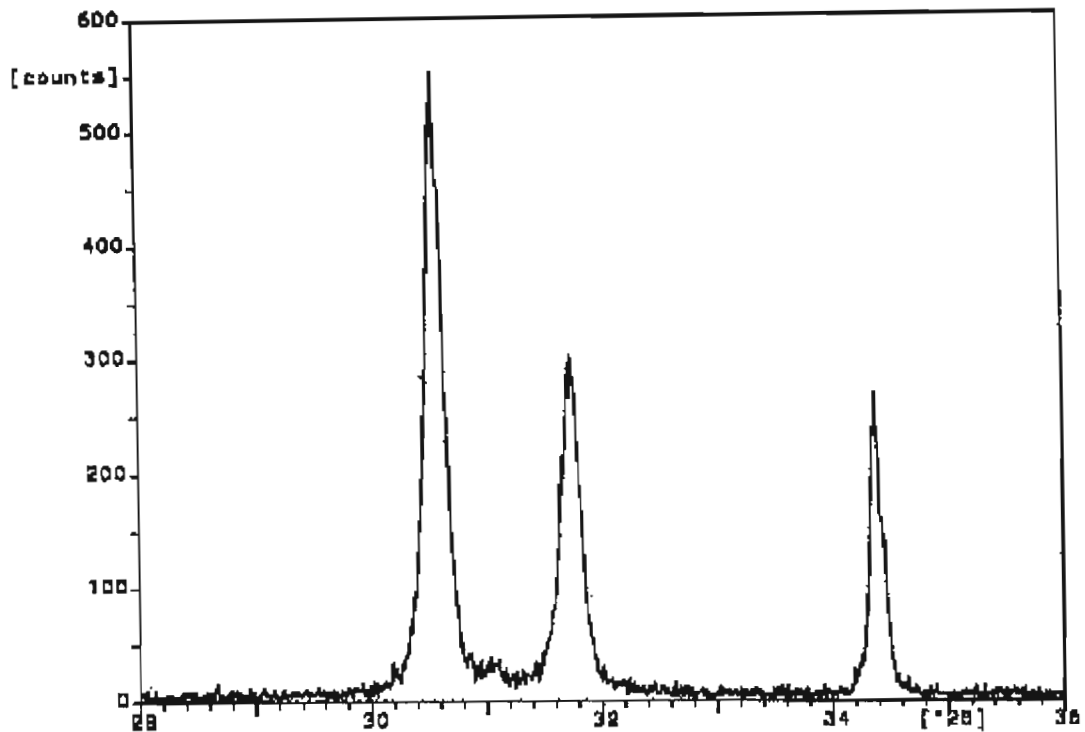


Fig. AE1 – X-Ray Analysis Graph

A monochromatic beam of X-rays ( $\text{Co } k_{\alpha}$ ,  $\lambda = 1.7889 \text{ \AA}$ ) was directed onto the sample and the angle ( $2\theta$ ) and the intensity of the diffracted beams measured. The lattice spacings,  $d$ , were calculated from the  $2\theta$  values using Bragg's Law ( $n\lambda = 2d \sin(\theta)$ , where  $n$  is an integer). The  $d$  spacing and intensity data was compared with the ICDD (International Commission for Diffraction Data) database for phase identification. The x-axis of Fig. AE1 indicates the angle ( $2\theta$ ) at which the x-ray beams were diffracted. The y-axis gives the intensity of the diffracted beam.



```

Diffractometer type: PW3710 PASAD
  Tube anode: Co
Generator tension [KV]: 40
Generator current [mA]: 40
Wavelength Alpha1 [Å]: 1.78896
Wavelength Alpha2 [Å]: 1.79265
Intensity ratio (alpha2/alpha1): 0.500
  Divergence slit: 1/4°
  Receiving slit: 0.1
Monochromator used: YES

Start angle [°2θ]: 28.000
End angle [°2θ]: 36.000
Step size [°2θ]: 0.010
Maximum intensity: 543.8900
Time per step [s]: 5.000
Type of scan: SINE

Peak positions defined by: Top of smoothed peak
Minimum peak tip width: 0.00
Maximum peak tip width: 1.00
Peak base width: 1.00
Minimum significance: 0.75
Number of peaks: 4

```

Angle [°2θ]	d-value α1 [Å]	d-value α2 [Å]	Peak width [°2θ]	Peak int. [counts]	Back. int. [counts]	Rel. int [%]	Signif.
30.555	3.3947	3.4021	0.060	543	5	100.0	2.38
31.855	3.3414	3.3486	0.100	26	5	4.8	0.85
31.740	3.2710	3.2781	0.180	282	5	52.0	15.69
34.370	3.0274	3.0340	0.060	266	5	48.9	3.07

Fig. AE2 – X-Ray Analysis Results

Initially the angle range was 0 – 60° (with a step size of 0.04° and a time per step of 1 second) in order to establish qualitatively what the constituents of the precipitate were. This showed that aragonite and calcite were the main constituents. The angle range was then reduced to 28 – 36° (with a step size of 0.01° and a time per step of 5 seconds) in order to quantify the ratio of calcite to aragonite.

The strongest peak for calcite was obtained at a d-value of 3.035 Å whereas the strongest peak for aragonite is obtained at 3.397 Å. Fig AE2 indicates that the intensity of the strongest peak for aragonite was 543 counts and that for calcite was 266 counts. The intensity of the strongest calcite peak is known from the ICDD data to be twice that of aragonite.

Since the precipitate is made up of only calcite and aragonite,

$$100\% = \frac{I_c}{2} + I_a$$

where,  $I_c$  = intensity of calcite

$I_a$  = intensity of aragonite

$$\begin{aligned} \text{Therefore the amount of calcite} &= \frac{\left(\frac{I_c}{2}\right)}{\left(\frac{I_c}{2}\right) + I_a} (100) \\ &= \frac{\left(\frac{266}{2}\right)}{\left(\frac{266}{2}\right) + 543} (100) \\ &= 20\% \end{aligned}$$

Amount of aragonite present = 80%

The calcite/aragonite ratio of the constituents of other precipitates was obtained in a similar fashion.

## APPENDIX F

### Hardness Test Results

Atomic absorption was used to test the hardness of the feed and filtrate samples. Table AF1 indicates the results obtained for tests done for experiments testing the effect of temperature. Table AF2 indicates the results obtained for tests done for experiments testing the effect of flow rate.

Temperature (°C)	ppm Ca			% Ca Removed	
	filtrate with magnets	filtrate without magnets	feed	with magnets	without magnets
30	68	79	124	45	36
40	63	69	124	49	44
50	63	59	124	49	52
60	62	58	144	57	60
70	46	45	144	68	69

**Table AF1 – Hardness Test Results for Temperature Changes**

Flow Rate (m <sup>3</sup> /hr)	ppm Ca			% Ca Removed	
	filtrate with magnets	filtrate without magnets	feed	with magnets	without magnets
150	63	69	124	49	44
200	42	59	159	74	63
300	38	48	157	76	69
400	21	46	188	89	76

**Table AF2 – Hardness Test Results for Flow Rate Changes**

Hardness (ppm Ca) indicates the concentration of  $\text{Ca}^{2+}$  ions in the solution. Therefore the amount of calcium removed (as a precipitate) is equal to the difference between the hardness of the feed and the filtrate samples.

$$\text{Amount of Ca removed} = (\text{hardness of feed}) - (\text{hardness of filtrate})$$

$$\% \text{ Ca removed} = \frac{(\text{hardness of feed}) - (\text{hardness of filtrate})}{(\text{hardness of feed})} \times 100$$

*Therefore for temperature = 30 °C (with magnets)*

$$\begin{aligned} \% \text{ Ca removed} &= \frac{124 - 68}{124} (100) \\ &= 45\% \end{aligned}$$

The other results for % Ca removed were similarly obtained.