INVESTIGATION OF ANTI-FOULING PROCESSING AIDS IN THE PRIMARY EVAPORATION OF WHEY PERMEATE

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DYLAN HARRISON

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Abstract

The production of lactose via the concentration of whey permeate is an important process in the dairy industry. Hautapu dairy factory, owned by Fonterra Co-operative Group, process milk into a range of dairy-based products including; Cheese, Milk Protein Concentrate and Lactose. This project was focused around reducing fouling during the evaporation of whey permeate for the production of lactose powder. As whey permeate is heated in evaporators, mineral salts precipitate and accumulate onto the stainless steel heat exchange surfaces. This layer of mineral scale, known as fouling, greatly reduces the amount of heat transfer used for evaporating the whey permeate. Once the fouling gets to a point where it is no longer achievable to reach the concentrated solids target, the evaporator is shut down and cleaned with chemicals to remove the scale build up.

To decrease the amount of scale build up, a process aid is added to the whey permeate. This process aid "A", or PAA, is a polyphosphate that when added to the feed stream gives longer run times. This project was aimed at establishing the chemistry behind the inhibiting abilities of PAA and its interaction with whey permeate. It is known that PAA acts as a complexing agent with calcium when it is added to the permeate stream which prevents it from forming calcium phosphate, the main source of fouling.

In the course of the research, it was fortuitously discovered that PAA works very inefficiently as an inhibitor in whey permeate because of its ability to form an insoluble salt with free calcium ions. The consequence of this was that high calcium levels in whey permeate lead to PAA precipitating out of solution rendering it an ineffective anti-fouling agent to prevent further scale build up. As a result of this, alternative inhibitors were considered and tested for their calcium tolerance and calcium phosphate inhibiting properties. From these considerations, carboxymethyl inulin was regarded as the most favourable replacement candidate for PAA. This resulted in plans being set down for a future industrial trial involving the carboxymethyl inulin.

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It is these people I would like to thank for all of their guidance, support, knowledge and assistance:

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List of Abbreviations

ΔT	Temperature difference
Ca-ISE	Calcium – Ion Selective Electrode
CIP	Cleaning in Place
CMC	Carboxymethyl Cellulose
CMI	Carboxymethyl Inulin
DRP	Dissolved Reactive Phosphate
HEDP	1-Hydroxy Ethylidene-1,1-Diphosphonic Acid
FSANZ	Food Safety Australia New Zealand
FTIR	Fourier Transform Infrared Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IUPAC	International Union of Pure and Applied Chemistry
MPC	Milk Protein Concentrate
MVR	Mechanical Vapour Recompression
PAA	Process Aid "A"
PMA	Polymaleic Acid
RDR	Recommended Dosing Rate
RO	Reverse Osmosis
SEM/EDX	Scanning Electron Microscope/Energy Dispersive X-ray
SHMP	Sodium Hexametaphosphate
SPP	Sodium Polyphosphate
TP	Total Phosphorus
TS	Total Solids
TVR	Thermal Vapour Recompression
UF	Ultra-Filtration
WPC	Whey Protein Concentrate

Chapter 1: Project Overview

1.1 Problem Definition

Lactose manufacturing has become an important part in the New Zealand dairy industry. Fonterra processed over 13.86 billion litres of milk over a 14 month period to July 2008 (Fonterra, 2009). Lactose is used mainly to standardise other dairy products and is sourced from whey, which is a by-product from cheese and casein manufacturing. Previously whey was dumped or fed to pigs but is now refined for the production of whey proteins and lactose.

The production of lactose involves removing proteins from the whey via ultra-filtration (UF), then concentrating up the permeate solution via steam-assisted evaporation before the lactose is crystallised out then separated and dried. One of the issues with concentrating whey permeate is that it forms insoluble salt minerals that can build up on heat exchange surfaces causing a significant decrease in thermal energy transfer that is required for evaporation.

Fonterra Hautapu manufacture lactose powder from whey permeates. To help prevent the build up of minerals on their heat exchange equipment a processing aid is added called Process Aid 'A' (PAA). This is alleged to give longer run times and slow down the rate of fouling. There is evidence from long time operators to suggest that PAA works, with an increase of on-product run times from 7 hours to 20 hours.

Fouling is a major problem in the dairy industry and it is not exclusive to lactose manufacturing. The fouling seen in whey permeate evaporators is different to the type of fouling usually seen in other dairy evaporators due to the lack of protein. Protein has been widely regarded as a major contributor to fouling (Bansal & Chen, 2006; Daufin *et al.*, 1987; de Jong, 1997; Jun & Puri, 2005; Prakash *et al.*, 2005; Simmons *et al.*, 2007; Visser & Jeurnink, 1997) but since nearly all protein is removed during the UF process only mineral fouling is observed.

The reason fouling is such an issue is due to the loss of efficiency in energy use. When fouling occurs the layer between the heating medium and the product thickens causing a reduction in temperature difference (ΔT) of the steam side of and the product side the evaporator. This means that more heat has to be added to the system in order for the product to be kept at operating temperature. Once fouling gets too heavy and the heat needed to keep the evaporator running at constant temperature is too great, the plant is then shut down for cleaning in place (CIP) to remove the mineral scale before it can be started up again.

1.2 Project Objectives

During the course of this project objectives initially conceived at the outset changed due to the development of new findings and a better understanding of the chemistry of PAA. Final project objectives deviated significantly from those initially outlined. Therefore, the project evolved from an initial and intense focus on how to detect fouling, to the interaction of PAA and calcium ions and then finally to a search for better alternatives to PAA.

1.2.1 Initial Objectives

The main objective of this project was to optimise the use of PAA in the Holvrieka evaporator at Fonterra Hautapu's Lactose plant. The typical dosing rate of PAA as used at Hautapu is 0.4% w/w but it was not established if this was the correct dosing rate for its purpose of use. The initial objectives to optimising the dosing rate and to further investigate fouling included:

- Ascertaining if the fate of PAA could be detected throughout the primary evaporator processes.
- Attempting to replicate the conditions similar to those in the evaporator.

- Recreating fouling on a laboratory scale to determine the optimal dosing rate and looking at optimising the current dosing rate for any financial benefits.
- Establishing the chemistry behind PAA and its interaction with whey permeate.

To achieve these objectives, analytical techniques needed to be identified that could be used to determine the chemistry of PAA with whey permeate. Analytical techniques that could detect calcium and orthophosphate were of importance as these were determined to be the main components that contributed to whey permeate mineral fouling.

For initial objectives three analytical techniques were employed. Ion Coupled Plasma – Mass Spectrometry (ICP-MS) was used for elemental composition, Calcium Ion Selective Electrode (Ca-ISE) was used for free calcium ion levels and Dissolved Reactive Phosphorus (DRP) was used to measure the orthophosphate levels. These techniques, which will be discussed in Chapter 3, along with other complications, led to the discovery of the chemistry behind PAA and calcium ions in aqueous solution.

This discovery led to the development of the chemistry of PAA with calcium ions and caused the project to develop further. From here the project looked more at a simplified system that focused on PAA and calcium ions in an aqueous solution without the presence of whey permeate. New objectives were set out and new analytical techniques were employed. The new objectives involved:

- Identifying the characteristic properties of PAA.
- Finding the point at which calcium levels have an effect on the precipitation of PAA.
- Gaining a clearer understanding of how calcium ions interact with PAA.
- Identifying any pH effects on the precipitation of PAA with calcium ions.

For these objective new analytical techniques were used. They included a Scanning electron microscope (SEM), Infrared Spectroscopy (IR) and a pH-stat meter coupled with turbidity measurement. These instruments gave a clearer understanding of the chemistry of PAA. The conclusion that PAA was potentially ineffective as an inhibitor led to the final part of the project that has looked at alternatives to PAA that are proposed to provide better performance as a mineral fouling inhibitor.

1.2.2 Final Project Objectives

As the project developed, new discoveries were made regarding the chemistry of PAA. These findings resulted in new objectives that were focused on alternative chemical products that could be used in replace of PAA in evaporators. It was important that the alternatives met certain criteria to be eligible for use in whey permeate evaporators. These specifications give a range of criteria, which include:

- A readily available source from a supplier
- An amount available to use on an industrial scale
- Economically beneficial over PAA
- Able to be implemented into dairy factories without heavy alteration to existing plants

From a range of different anti-fouling agents, it was important to find out what interactions they had with calcium ions in terms of precipitation, as this is what was considered to be one of the limiting factors of PAA performance. The objectives for this last part of the project were:

- Finding alternatives to PAA that meet the criteria stated above, including thermal stability, calcium tolerance and food safety
- Assessing the best alternative for the use in the Holvrieka evaporator for a scaled up plant trial

The final stages of this project were focused on selecting a suitable replacement for PAA as an anti-fouling agent for use in whey permeate evaporators for Fonterra. As part of an industrial project it was important to find out what the financial benefits would be in using an alternative as well as setting out plans for an eventual plant trial that was intended to be executed at a Fonterra dairy plant.

All valuable objectives were realised albeit not relating to the initial hypothesis. The most important aspect was that the chemistry of PAA and whey permeate were better understood. This was achieved with the surprising outcome of PAA being potentially very ineffective and it has also opened new research into finding a better solution to the problem of mineral fouling in whey permeate evaporators as will be explained later in this thesis.

Chapter 2: Introduction to Lactose Manufacturing and Mineral Fouling

2.1 Introduction to Lactose Production

The production of lactose has become an important aspect in the dairy industry. It is used for the standardisation of milk products such as powders and infant formulas, it also has applications in the pharmaceutical industry as a tablet filler. Lactose production in New Zealand has become an important and profitable process since the establishment of the company, *Lactose New Zealand* in 1914. Today's manufacturing environment centres around lactose from whey, which is a far cry from the times when whey was considered a waste product from manufacturing of cheese and was fed to pigs or spread on farms.

Lactose is a disaccharide sugar most notably found in mammalian milk. The primary source of lactose is from bovine milk. Other non-mammalian sources of lactose are rare such as the pollen of the Forsythia flowers (Takahiro *et al.*, 1991) and Sapotaceae plants (Reithel & Venkataraman, 1956). In mammals it is biosynthesised via an anabolic pathway in the mammary gland during lactation. Bovine milk consists of 4.8% lactose, by weight as shown in Table 2-1, of total composition.

Table 2-1: The major components of bovine milk

Component	Concentration / % w/w
Water	87.1
Fat	3.95
Protein	3.30
Minerals	0.67
Organic acids	0.18
Lactose	4.8
Vitamins	<0.001

2.1.1 Properties and Uses of Lactose

Lactose belongs to a group of natural elements called carbohydrates. They were originally perceived to be "hydrated forms of carbon" having a general formula $C_x(H_2O)_x$. This was later found to be incorrect but the name has endured. The disaccharide sugar, which can technically also be labelled as an oligosaccharide, is made up of two monosaccharide units covalently bonded through a β 1 → 4 glycosidic linkage.

The two monosaccharides are β-Galactose and Glucose. Both of these aldoses are in a pyranose ring formation and are D-enantiomers. This gives rise to its International Union of Pure and Applied Chemistry (IUPAC) name; β-D-Galactopyranosyl-(1 → 4)-α/β-D-Glucopyranose. Figure 2-1 shows lactose in its $^4C_1$ chair formation for both units. Galactose and glucose differ by the hydroxyl group on carbon 4, where the hydroxyl group is axial on Galactose and equatorial on Glucose.

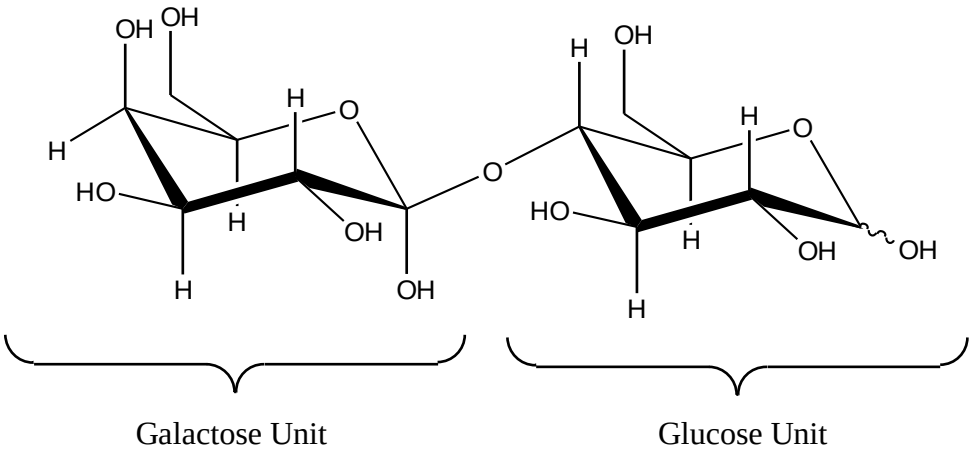


Figure 2-1: Molecular structure of lactose showing the galactose and glucose unit

Figure 2-1 shows the molecular structure of lactose, the squiggly line denotes that the hydroxy group can either be facing down (α- position) or up (β- position). The two forms of α- and β-anomers differ in their physical properties (Table 2-2) which can lead to different commercial applications. When α-lactose crystallises,

a water molecule is also associated, this water of crystallisation gives rise to the common name of monohydrate lactose.

Table 2-2: Physical properties of α-lactose and β-lactose (Packer *et al.*, 1998)

Property	Units	α-lactose	β-lactose
Molecular weight	Da	360.3*	342.3
Melting point	°C	202	252
Density	g mL^{-1}	1.545	1.59
Specific optical rotation	α^{20}_{589}	+91.1	+33.5
Heat of Solution	J g^{-1}	-50.24	-9.62
Solubility in water at 20°C	g/100mL	7.4	50.00

* for the monohydrate form of crystalline α-lactose

When lactose is dissolved in water, mutarotation occurs. This is where the two forms of lactose interconvert to produce a solution of 62.7% β-lactose at 20°C at equilibrium. α-lactose is a far less soluble species so the concentration of solution results in α-lactose precipitating out and further mutarotation takes place to maintain the same equilibrium. Figure 2-2 illustrates the solubility of the two lactose forms at a given temperature.

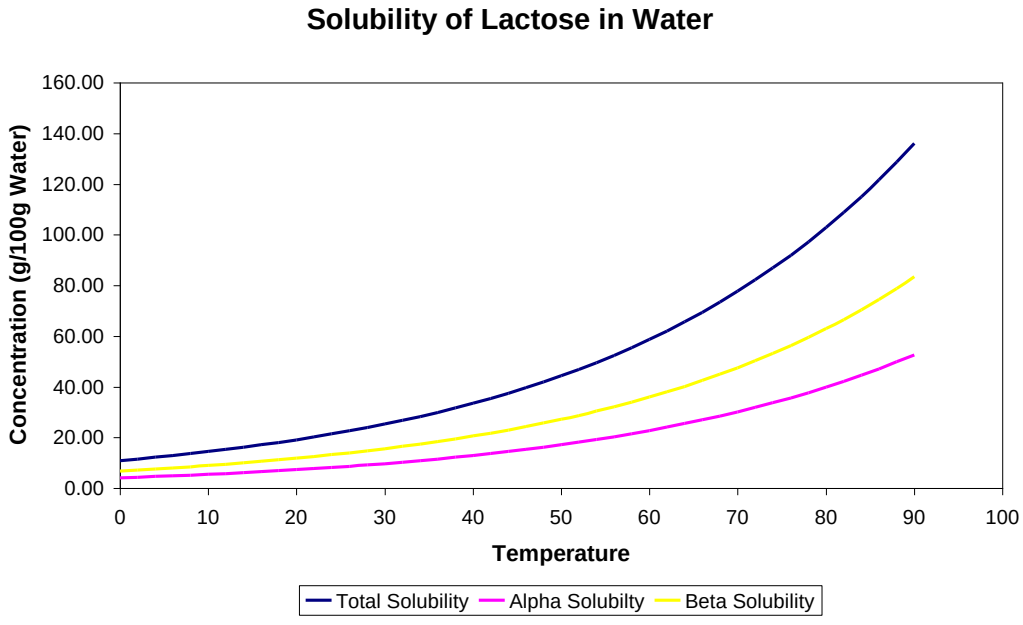


Figure 2-2: Solubility curve of lactose in water relating to temperature

Today lactose is used in the food and confectionery industries. It has about a 30% lower sweetness than sucrose and is used as a binder of flavours and aromas. Another important application of lactose is in the production of infant formula. Human milk contains 7% lactose, compared to ~4.8% in bovine milk so the lactose is added to cow's milk for standardisation.

Pure α-lactose is used in the pharmaceutical industry as filler and binder in tablets, capsules and other oral product forms such as inhalers. It is a compound that is chemically inert and it also protects and enhances any aspect of the safety of the drug, whereby the active ingredient is not reactive to lactose that is present in the tablet (Packer et al., 1998).

It can also be used as a carbohydrate source for the production of ethanol. Lactose can be fermented using yeasts that produce lactase that can break lactose down in its mono-saccharides of glucose and galactose. These sugars are then broken down into ethanol and carbon dioxide.

2.1.2 Lactose Manufacturing

Lactose is manufactured from whey which is usually sourced from cheese manufacturing. Whey can either come from the separation of curds and whey to form cheese whey or it can come from casein production. Casein is produced via two methods. Casein can be produced by adjusting the pH of milk with sulphuric acid to precipitate out casein protein at its iso-electric point; this is known as acid casein. The other method is via an enzymatic pathway where rennet is added which precipitates out the casein. Milk can also be passed through an ultrafiltration membrane to separate out and concentrate milk proteins which is sold as Milk Protein Concentrate (MPC) (Packer et al., 1998).

Whey that is used for the manufacturing of lactose is passed though an ultrafiltration (UF) membrane to separate out whey proteins that are left behind from previous processes. The retentate is evaporated and spray dried to produce

whey protein concentrate (WPC). The permeate, which is the solution that passes through the membrane, is only around 5% total solids, consisting mainly of lactose and ash. This overall process of the sources of whey permeate are shown in Figure 2-3. The permeate is then concentrated and refined, as illustrated below, for the production of lactose powder.

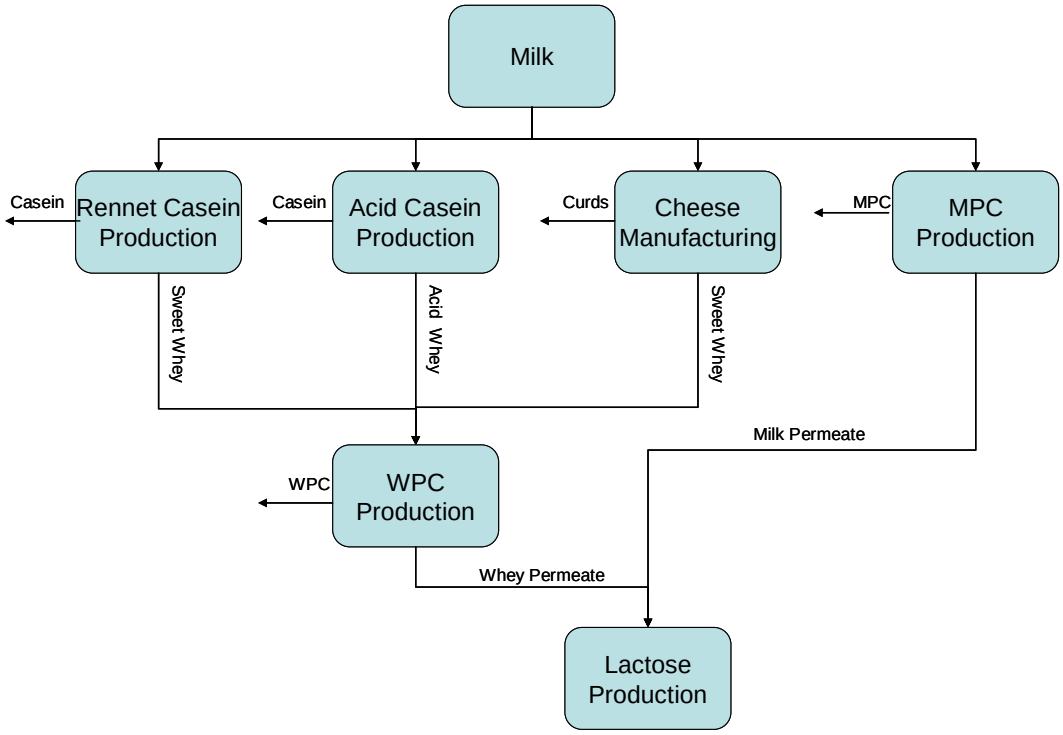


Figure 2-3: Sources of ultrafiltrated permeate for the production of lactose

The first step in concentrating whey permeate is by reverse osmosis. Reverse osmosis membranes have a much smaller pore size than UF membranes, which is permeable only to water. In a water-permeable membrane, water tends to move into the solution of higher salt concentration in a process called osmosis, to balance out the concentration of solutions. This process can be reversed by applying a large pressure to the more concentrated side, illustrated in Figure 2-4. This forces the water back the other way through the membrane hence the term, "reverse osmosis". This process will concentrate the permeate to around 15 – 20%.

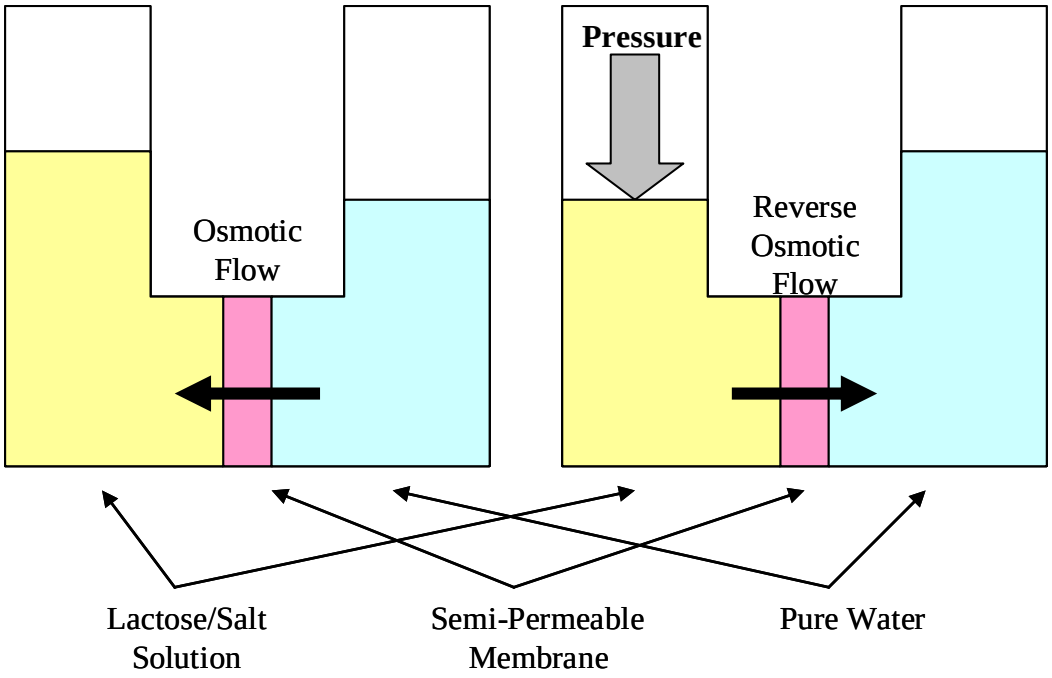


Figure 2-4: Basic schematic of the principal of reverse osmosis

The next step of concentration is via evaporation. At Hautapu dairy factory there are three permeate evaporators. These all operate at different temperatures in order to keep the lactose soluble as the total solids of the solution increases during the evaporative process. The first evaporator is known as the Holvrieka evaporator. This is the primary evaporation step and is a mechanical vapour recompression (MVR) falling film evaporator. Although it has five calandrias and multiple passes, it is effectively a single effect evaporator running at approximately 69°C. The Holvrieka evaporator increases the concentration from 15-20% up to 50% total solids. This evaporator is the main step in the manufacturing process that is of concern to this project.

The other two evaporators at the Hautapu permeate plant are the Weigan secondary evaporator and the final crystallising evaporator. The Weigan is a thermal vapour recompression (TVR) evaporator running at an operating temperature of ~69°C. This increases the solids content from 50% to 62% total solids. When solids percentage reaches a value of around 70%, solubility becomes difficult due to the availability of the water to maintain the lactose in solution. The crystallising evaporator (the third evaporator in the process) promotes crystal growth on existing nuclei and allows the crystals to grow in the

separator so that the total solids can still increase without causing further nucleation. Too much nucleation can result in smaller crystal size that is difficult to separate from the bulk solution.

When the solids have reached the desired targets the solution is then transferred to large crystallisers for cooling. This is a batch process where the solution is cooled down to 10°C via a water jacket. Cooling is done slowly over a period of time to allow crystals to grow as the saturation point is lowered. If rapid cooling was to take place then the solubility of the lactose would decrease, therefore the saturation point would lower at a rate faster than the rate of crystal growth causing nucleation. Nucleation is also referred to as "showering" out of solution, which is undesirable. Once the temperature has been lowered to the point where crystal size is optimum then the lactose crystals can be separated from the remaining solution.

The crystals are separated from the solution, which is at this stage called "mother liquor", using a decanter. Decanting is a process of separating solids from solution by settling out particles. Crystal size here is therefore important, as small crystals can be lost in the decanter process due to their small size causing them to be suspended in solution as they do not settle out. The mother liquor contains minerals such as calcium salts, that are suspended in solution due to their small size, as well as some non-recoverable lactose that is still dissolved. To remove impurities the crystals must be washed. Refining crystals involves washing them with cold water. This dissolves the outer layer of crystals where impurities are adsorbed before the crystals are sent for final drying. A centrifuge is used to remove the wash water that was added during the refining process. This wash water is sent back through the evaporation process to recover the dissolved lactose. After separation, the crystals are carried forward where they are dried and packed in the bag house. The overall process from whey permeate to lactose powder is shown in Figure 2-5.

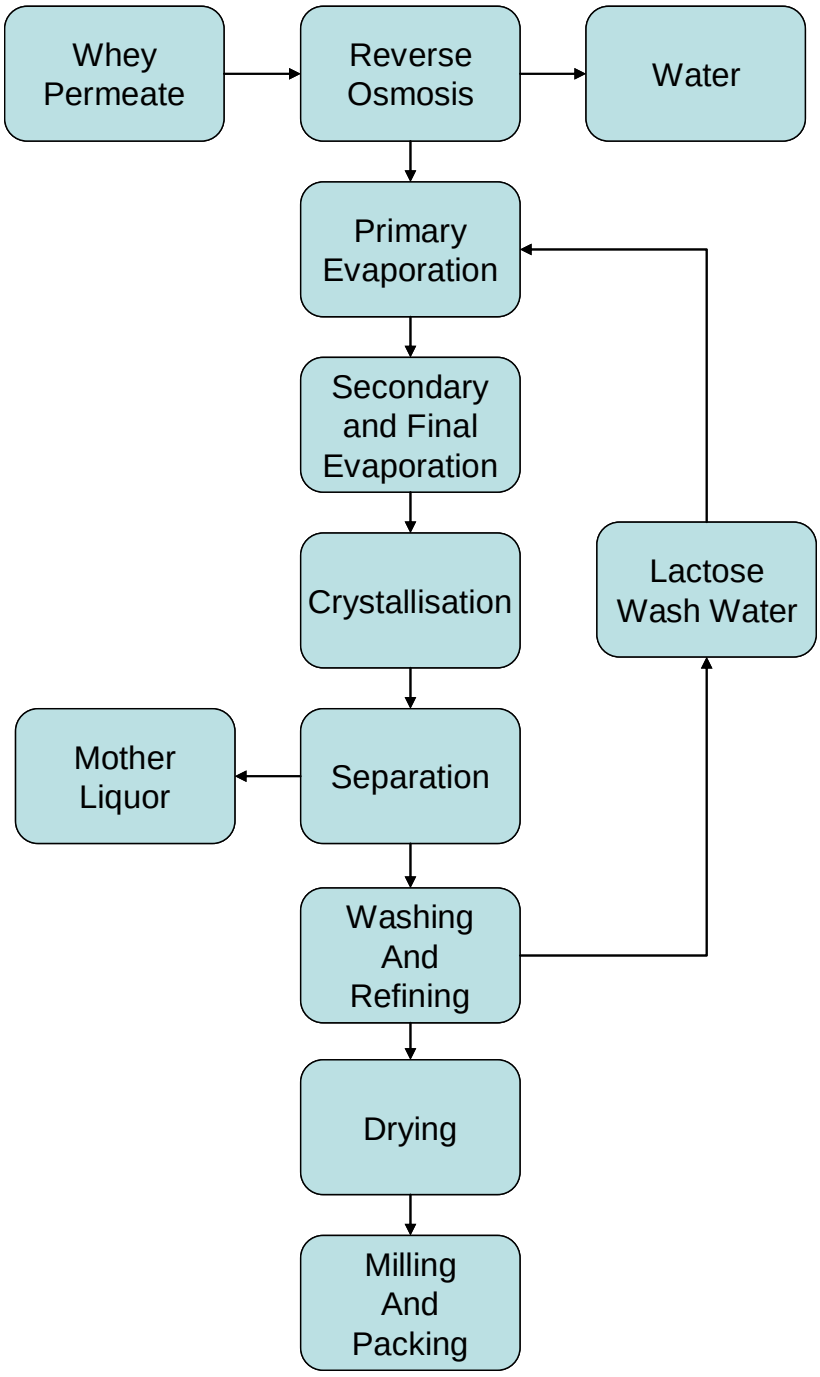


Figure 2-5: Step-wise process for the production of lactose powder

2.2 Deposition of Minerals in Dairy Processes

Fouling in the manufacturing of dairy products is a major problem and is often the limiting factor in continuous dairy processing. Lactose manufacturing is unique in terms of dairy processing because of its low protein content. A review by Jun

(Jun & Puri, 2005) suggested that mineral fouling can become dominant in milk and other protein rich dairy products but only at higher temperatures above 90°C. Morrison (Morison & Tie, 2002) mentions that mineral fouling can occur at lower temperatures but only when the mineral to protein ratio is high.

Due to the low protein content in whey permeate, mineral fouling is different to that usually seen in the dairy industry. Protein is a major component in dairy fouling (Santos *et al.*, 2006; Visser & Jeurnink, 1997). Visser and Jeurnink conclude that even at room temperatures, as soon as protein-containing solutions come into contact with a metal surface then adsorption would take place. This initial adsorption was not thought to be the main component of fouling but it was regarded as necessary to initially modify the surface of the metal. The modified surface can then act as a basis for particulate matter of colloidal dimensions to attach itself to. This protein layer can build up entrapping further proteins, so increasing the fouling rate.

The majority of fouling literature in the dairy industry is centred around protein fouling (Bansal & Chen, 2006; Daufin *et al.*, 1987; de Jong, 1997; Rosmaninho *et al.*, 2007; Schraml & G., 1996; Simmons *et al.*, 2007) as protein along with fat are the two most valuable components of milk. Permeates are considered a by-product of ultrafiltration protein manufacturing and hence there has been less research done on this type of fouling. However there have been studies which focus exclusively on mineral fouling. It has been proposed that the fouling appears to act via a different mechanism. Morrison and Tie (Morison & Tie, 2002) speculated that the mineral fouling was due to precipitation occurring directly on the surface of the metal rather that adsorption of the precipitate originally generated in the bulk solution. This would account for his findings that suggest keeping the calcium and the orthophosphate as dissolved ions in solution would promote fouling, but precipitating it out in the bulk solution would reduce the severity of mineral build up on the surfaces that would be fouled in such an environment.

2.3 Current Fouling Solutions

When dairy plants reach a certain point where the fouling is too severe, production is halted and the plant is cleaned. The reason for cleaning a permeate plant is two-fold. The first is to keep the plant sanitary so that microbial bugs do not grow and contaminate the final product. The second is to improve the plant's performance.

Fouling can reduce the amount of heat transferred from the steam side of the stainless steel to the product side. The removal of this fouling re-exposes the stainless steel to the product where better heat transfer can take place. To remove this foulant a process known as cleaning in place (CIP) occurs.

CIP is where chemicals are used to clean the plants of fouling and to keep the plant sanitary. A usual CIP for whey permeate evaporators usually entails an initial water flush to remove any product that may still be in the evaporator. The next step is to do an acid flush. Nitric acid is used at a strength of approximately 1% by volume. This removes the scale build up from the stainless steel. The acid is first flushed through the evaporator and more acid is then recirculated through the evaporator until the product has been removed. A caustic flush can also be performed for the removal of proteins but in whey permeate evaporators this is not always needed due to the low levels of protein. For Hautapu dairy factory PAA is added to lengthen runtimes so that the plant does not have to undergo CIP as often.

2.3.1 Polyphosphates: Description and Properties

Phosphates are defined by compounds which contain P–O linkages. Polyphosphates are a condensed form or chain of repeating orthophosphate ions with the general formula of $[PO_4^-]_n$. This form of polyphosphate has the ability to form soluble complexes with metal ions. Complexation of polyphosphates have been known for over 170 years and have been by reviewed by Rashchi and Finch within the past decade (Rashchi & Finch, 2000).

Polyphosphates can either be linear or form cyclophosphates. Liner phosphates can have chain lengths up to ca.18 for commercial sodium salt glasses. Laboratory prepared polyphosphates can reach up to ca. 3000 phosphorus atoms per average chain length.

The main two types of polyphosphates relevant to this study are sodium hexametaphosphate, which is the trade name that is given to PAA, and straight chain polyphosphates. Since PAA was also called sodium hexametaphosphate it was not unrealistic to assume that PAA contained six phosphate groups, but this turns out to be an incorrect form of nomenclature name used in industry.

For sodium hexametaphosphate (SHMP) the main linked chain is a series of six orthophosphate groups covalently joined via the P–O bond to form a cyclic ring, Figure 2-6. The other polyphosphate, Sodium Polyphosphate (SPP), polymerises linearly but with an unknown number of repeating units, Figure 2-7. The formula is $[PO_4^-]_n$ with the orthophosphate group repeating usually ca. 18 units for commercial grades but can reach up to ca. 3000 for laboratory grades.

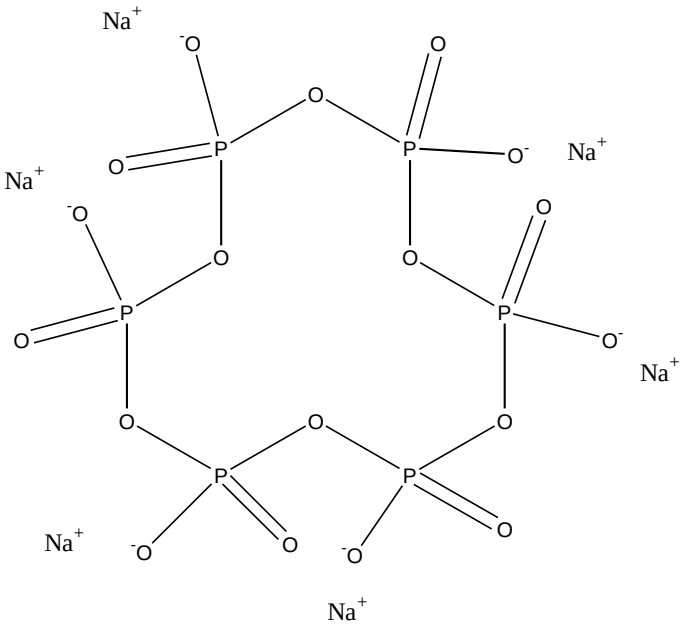


Figure 2-6: Molecular structure of sodium hexametaphosphate

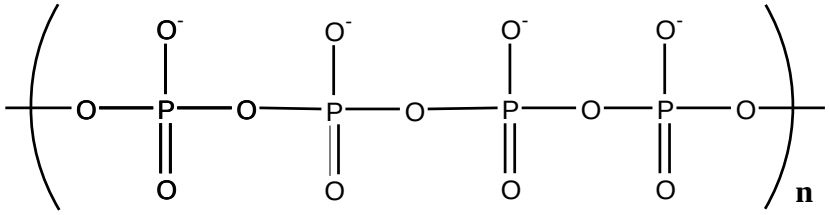


Figure 2-7: Molecular structure of polyphosphate

2.3.2 Use of Polyphosphates in Industry

Soluble chain polyphosphates have traditionally been used for the treatment of hard water to prevent the growth of calcite crystals blocking pipes. It is believed that the polyphosphate can adsorb onto the crystal to prevent further growth at a sub-stoichiometric level. This is believed to be where the use of PAA in industry comes from as it is also effective in water systems against other insoluble calcium salts.

Polyphosphates are also used in the meat industry to prevent the coagulation of blood. Previously sodium citrate was used but caused adverse precipitation of fibrin (an insoluble protein). Polyphosphates have also found uses in food technology. Calcium diphosphates (diphosphates are also known as pyrophosphates) are used as polishing agents in toothpastes and sodium diphosphate is an ingredient in making instant pudding.

PAA has been used as a processing aid at Hautapu dairy factory since 2001. An "in-house" trial was conducted which compared triphosphate and hexametaphosphate, the latter of the two has been discovered as a result of this project to actually be polyphosphate. The hexametaphosphate/polyphosphate provided longer run times on product so was chosen as the new processing aid "A" for whey permeate evaporation.

Chapter 3: Method Development for Fouling Deposit Analysis and Fouling Replication

3.1 Introduction

For an accurate depiction of the fouling mechanism in evaporators it was important to isolate key variables which affect the severity of fouling. To single out these variables, a replication of the fouling process on a laboratory scale was proposed in the initial stages of the project. At that point of the project it was considered important to understand how fouling worked and what were the factors that contributed to mineral scale build-up.

A direct approach of PAA analysis was also proposed. This was to involve taking samples at the end of each calandria to measure directly the levels of PAA. This was also important as it could be used to justify any findings that may have come from the laboratory scale rig to see if a relative comparison could be made for the fate of PAA.

These two approaches of determining the role of PAA were to be combined to give a model of the interaction of PAA with whey permeate. This was then going to be used to find the optimum dosing rate which would then have been trialled in the dairy factory. As will be discussed, these initial objectives did not come to fruition for reasons to be outlined in this chapter.

3.1.1 Fouling at Hautapu Dairy Factory

To get an ideal representation of industry fouling it was important to identify the factors that contribute to evaporation, as this could be applied and used as a comparison for laboratory work. Temperature is the most obvious factor in effecting evaporation. For the laboratory scale fouling rig to work successfully it needed to operate at the appropriate temperatures. Composition of the whey

permeate feed stream was also important so it could be used to determine the rate of fouling. The difficulty of a bench scale fouling rig is the ability to achieve the industrially equivalent rate of evaporation of the permeate. Industrial evaporators concentrate permeate from 15% TS to 50% TS and this would be difficult to obtain in the same time frame on a bench rig due to the difference in heating media used. The industrial setting makes use of a Holvrieka evaporator as described below whereas the bench setup for replicating this would use water or a heated element as the source of the heating medium.

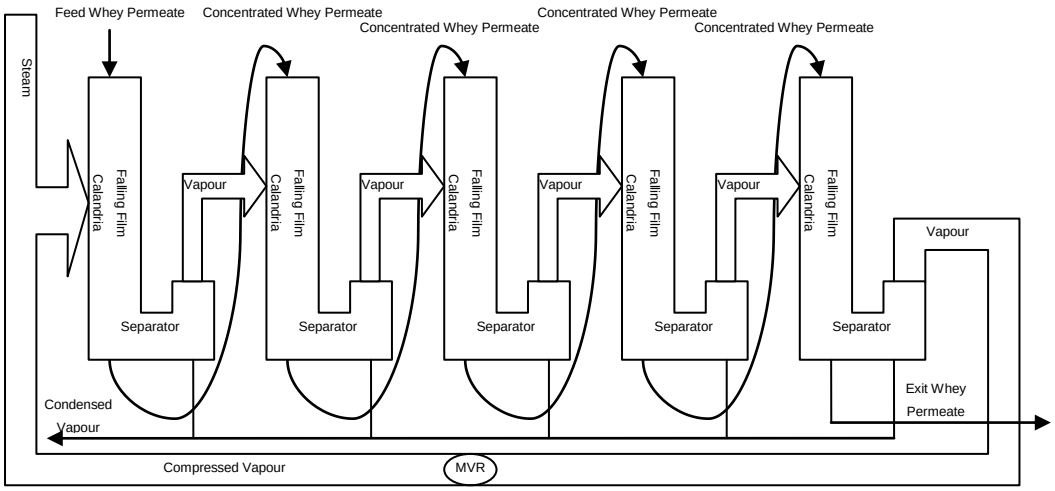


Figure 3-1: Typical layout of an MVR evaporator

The Holvrieka Evaporator as used at Hautapu is an MVR evaporator and shown in Figure 3-1, which is a multiple pass single effect falling film evaporator. It has seven "calandrias" that contain the product and steam. The calandria consists of a vessel containing multiple pipes where the product passes through, with steam that is used as the heating medium on the outside of the piping contained in the calandria vessel itself. The product is introduced into the calandrias at the top where it meets a distribution plate. This plate spreads the product evenly over the piping. As the product falls, vapour is produced from evaporation. This vapour forces the product against the walls of the tubing where it is more efficiently heated from the stream on the outside.

The temperature of the product in the evaporator is kept at 69°C. This is controlled by the amount of steam that is let into the system and the power output

of the steam fans that recycle the generated vapour from the product. This form of vapour recycling is known as Mechanical Vapour Recompression, or MVR. The vapour that is generated from the product is compressed via fans. This raises the pressure of the vapour and hence raises temperature. The two equations which relate to this function are:

Equation 3-1: Ideal gas law

$$PV = nRT$$

Where P is the pressure in Pascal, V is the volume in cubic metres, n is the amount of gas in moles, R is the gas constant in J mol^{-1} K^{-1} and T is the thermodynamic temperature in Kelvin. The main relationship in Equation 3-1 is that the pressure is proportional to temperature therefore increasing the pressure will cause an increase in temperature. The second equation relates to the energy output that can be generated by compression of the vapours. Equation 3-2 represents the theoretical energy consumption of the compression fans.

Equation 3-2: Theoretical energy consumption

$$E = Q \times (H_2 - H_1)$$

Where E is the total theoretical pumping energy, Q is the mass of vapours passing through the compressor and H_1 and H_2 are the total heat content of unit mass of vapours, respectively upstream and downstream of the compressor fan. The energy consumption is controlled by the output of the steam (H_2) so energy of the fan needs to increase when the amount to heat required is greater.

The power of the fan output is a good indicator of fouling. The fan speeds are dictated by the temperature of the product. When the fouling layer builds up on the heat exchange surfaces there is a reduction in the amount of heat that can be transferred from the steam side to the product side. To counteract this reduction of heat transfer, the speed of the compressor fan is increased. This raises the temperature of the steam to keep the product temperature constant. When the fan speeds have reached 100% capacity then the fouling layer is too great. Production

is then halted and the evaporator is taken 'off-product', (an in-house term meaning time when the evaporator is not concentrating whey permeate), so it can be chemically cleaned.

As the fouling layer on the piping grows there is a reduction in heat transfer. This is because fouling deposits act as insulators. Calcium salts have poor thermal conductivities compared to metals such as stainless steel. Table 3-1 shows how the resistance of the heat flow is greater when there is a wall of fouling material that is building up on the evaporators.

Table 3-1: Thermal conductivities of selected foulants and metals (Bott, 1995)

Material	Thermal Conductivity (W/m.k)
Biofilm	0.6
Calcium Sulfate	0.74
Calcium Carbonate	2.19
Copper	400
Mild Steel	27.6
Stainless Steel	15

The primary source of mineral fouling in the dairy industry is calcium phosphate. Panova (Panova, 2001), studied the precipitation of whey permeate minerals as carried out in New Zealand Dairy factories (specifically Kiwi Dairies and Edgecumbe) and found the main component to be a poorly crystalline hydroxyapatite phase of calcium phosphate along with a small amount of protein and citrate present in the solid. Calcium phosphate has a reverse solubility meaning that it becomes less soluble at higher temperatures. In acidic conditions, it dissolves completely and can be precipitated out of whey permeate by raising the pH.

Hence, any action that can be taken to provide longer 'on-product' time as well as keeping the evaporator running efficiently is regarded as an economic benefit to Fonterra. Longer run times mean that the plant can be in production mode for a

greater length of time and have a shorter downtime where the evaporator is being cleaned. It also has the benefit of reducing the amount of cleaning chemicals used if the intervals between CIP's are longer. The reduction of cleaning chemicals will not only have an economic benefit, but will also be beneficial to the environment, by reducing the amount of nitrates and other cleaning products.

As an attempt to provide better run times, Fonterra Co-operative Group Limited added a processing aid into the feed stream. This Process Aid "A" or PAA has been used since 2001 and has been perceived to provide longer run times from 8 hours up to 20 hours based on plant operator's experiences. The dosing rate that has previously been used was 0.4% PAA by weight of total solids in the feed stream. Table 3-2 shows the final diluted concentration of PAA in the feed stream, for example, at 20% total solids the PAA concentration is 800 ppm at a dosing rate of 0.4%. This data was calculated by measuring the amount of total solids going into the evaporator (usually 17 – 22%) and converting the dosing rate of PAA (usually 0.4%) as a weight percentage, to parts per million (ppm). It was the original intention of the project that the laboratory scale fouling rig would be used as a way of determining the effects of changes to the dosing rate of PAA with a goal of optimising the amount of added PAA. As the project progressed this aim had to be changed in light of some results obtained from bench scale experiments which will be discussed in later sections. The table below shows that a varying amount of PAA is added, which is proportional to amount of total solids feeding into the evaporator and the dosing rate percentage that is set by the operators.

Table 3-2: PAA dosing rate concentrations

Total Solids %	**Weight of whey kg Total Solids**	**0.3% PAA ppm conc.**	**0.4% PAA ppm conc.**	**0.5% PAA ppm conc.**	**0.8% PAA ppm conc.**
17	5.88	510	680	850	1360
18	5.56	540	720	900	1440
19	5.26	570	760	950	1520
20	5.00	600	800	1000	1600
21	4.76	630	840	1050	1680
22	4.55	660	880	1100	1760

3.2 Fouling Replication

As an alternative to the direct measure of PAA in the evaporator, it was also proposed to measure the rate of fouling using a fouling rig set up in the laboratory. Two main rigs were proposed, the first was a simple rig designed to easily test the rate of fouling. The second rig was more complex and was proposed to more accurately and quantitatively test fouling on stainless steel.

There have been few investigations that have looked specifically at whey permeate fouling in the literature. Others that have worked on fouling rigs have been more concerned with dairy fouling that incorporated protein such as (Ramachandra *et al.*, 2005; Rosmaninho *et al.*, 2007; Santos et al., 2006; Schraml & G., 1996; Simmons *et al.*, 2007). A study done by Morison and Tie, (Morison & Tie, 2002) focused on mineral fouling and was the basis of the second rig. The fist rig's design, however, was mimicked from a simple design that was constructed by Ramachandra *et. al.*, 2005, (Figure 3-2). For their study they were analysing sample substrates that were coated with titanium nitride. The fouling rig that was used for this study was similar in design without the sample blocks. It was important that fouling occurred on the stainless steel rotating shaft as this is the type of surface that the permeate comes into contact with in the Holvrieka evaporator.

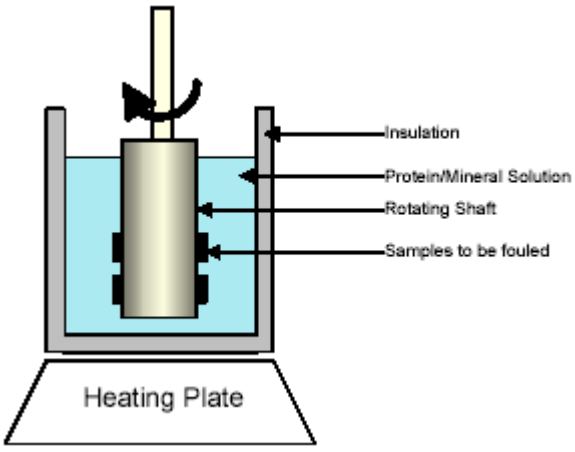


Figure 3-2: Ramachandra *et. al.* Fouling Rig

Figure 3-3: First Fouling Rig that was Used in the Present Study

The layout of the second fouling rig was more complex in nature and was designed around a flow-through chamber. This chamber was intended to give a laminar flow through the rig without any turbulence. This was worked out using specific calculations around the flow of product through the rig. The purpose of this was to keep a smooth flow through the rig without any turbulence that would result in uneven fouling. The calculations that were invoked are represented through Reynolds number calculations.

The Reynolds number is a dimensionless number that gives the ratio of the measure of internal viscous forces. It can be used to determine whether a flow of fluid is laminar, which is a smooth constant fluid motion, or turbulent, which can produce random flow fluctuations. Systems with low Reynolds numbers, Re > 2300, are considered to be laminar flow systems, while those with high Reynolds numbers, Re < 4000, are turbulent systems (ToolBox, 2005). The calculations for the Reynolds number in relation to this proposed fouling rig design are given in Appendix A.

Figure 3-4 shows the design for the second fouling rig. The original idea for this was to create a flow-through rig that was to be heated from an external source. Permeate was to flow through the rig while it was getting heated from the outside. It was thought that this action would induce fouling onto the stainless steel.

The rig was to have an internal tube that was blocked off with an outer sleeve which was going to be the subject of the fouling analysis. The outer tube was to be removable from the rig so that weight determinations could be carried out. The two end caps were to be fitted with distribution holes that were to give an even feed of permeate into the ring slit.

The permeate supply was to be transported via a peristaltic pump to ensure a constant flow regardless of its viscosity. A water bath would have been used as a pre-heater for the permeate so that by the time the solution had reached the end of the fouling rig it was at the correct temperature.

Much time went into the design of this rig but because successful fouling could not be achieved with the first initial rigs, for reasons explained later in this chapter, construction was abandoned and a new approach was taken into studying the effects of PAA on mineral fouling.

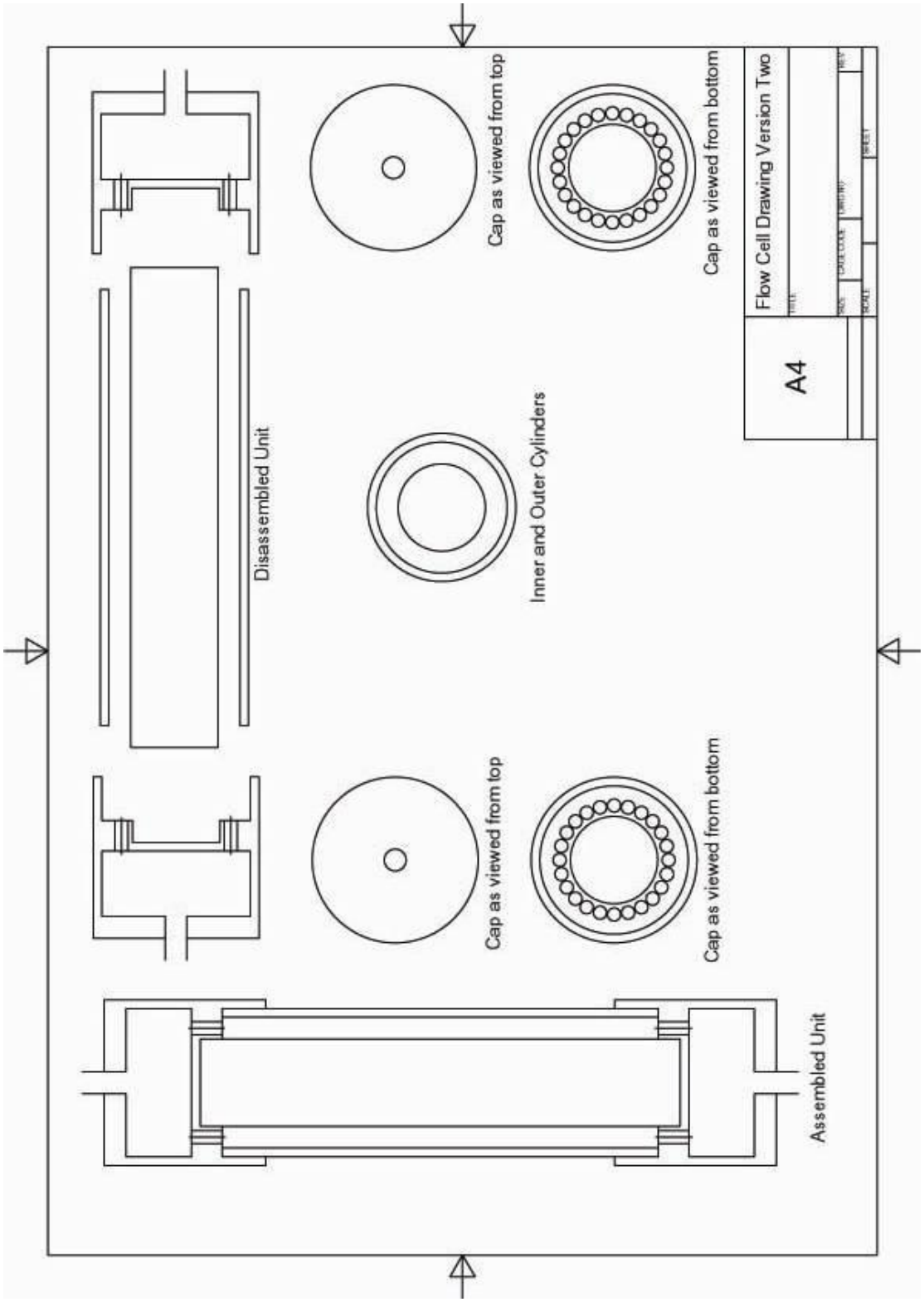


Figure 3-4: Design for second fouling rig

3.3 Fouling Rig Outcomes

Repeated attempts to cause mineral fouling using the first rotating cylinder rig proved difficult for a variety of reasons. The main factors that restricted fouling onto the rotating cylinder rig were heat transfer and permeate concentration. Permeate was heated to 70°C using a heating plate in a 5 L beaker. The stainless steel tube was submerged in the permeate where it was rotated for up to 8 hours. A very thin film of clear coating was seen on the cylinder that was easily wiped off under warm water.

It was hypothesised that because the heat into the system was coming from the bottom of the beaker via the heating plate, and not through the stainless steel (as it would be under industrial conditions) this was preventing fouling onto the stainless steel tube. To resolve this problem, a simple stainless steel fouling test was carried out. This involved the fabrication of a flat stainless steel circular plate with the diameter the same as the bottom of the beaker. This plate setup was used because it was envisaged that heat from the hotplate would have to travel through the disk to heat the permeate and hence would induce fouling on the plate in a similar manner to what would occur in evaporator pipes.

Tests on the stainless steel using this disk setup again resulted in the failure of any observable mineral fouling. The disk was left for up to 8 hours but the same film that was seen from the first rig was evident on the disk. Since the heat transfer should have been sufficient it was suggested that insufficient concentration of the permeate was another factor that contributed to the lack of fouling. The large amount of vapour that is produced as the permeate is concentrated is believed to be a major factor in fouling. The vacuum that is used to create boiling at 70°C is difficult to simulate on a bench scale. Replicating the conditions of an industrial evaporator is difficult on a laboratory scale. Getting the correct conditions, such as pressure and heat input is hard and also the rate of evaporation proved to be difficult in this case. This part of the project was hence abandoned and direct detection of PAA in whey permeate became the new focus of the project.

3.4 Instrumental Techniques used to study Whey Permeate Fouling

One of the initial approaches that was to be used for studying fouling was to quantify the level of calcium phosphate passing through the evaporator, since this is the main source of permeate fouling. It was intended to determine this by using three separate analytical methods. The first was Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), which determined the overall elemental concentration including total phosphorus (TP) and calcium concentrations. The second was a calcium ion-selective electrode (Ca-ISE) which would be used to determine the free calcium ion levels or more specifically the concentration of free unchelated calcium ions, $Ca^{2+}_{(aq)}$). The third method to be used was a UV/Vis based colourimetric technique that can be employed to determine the levels of orthophosphate, or dissolved reactive phosphate (DRP).

As the permeate travels through the evaporator it is concentrated by the evaporative process. This in turn increases the concentration of minerals. To account for this concentration effect in the whey permeate, a total solids calculation was performed on each of the sample points from which permeate was drawn for analysis. This was done by weighing an oven dried dish, the dish with the wet permeate sample and then the dish containing the oven dried permeate sample at 102°C overnight. The weights were then used to calculate the total solids by mass, shown in Equation 3-3. The results of this total solids calculation is shown in Table 3-3 below.

Equation 3-3: Total solids calculation

$$\%\, m/m\, Total\ Solids = \frac{Dry\ Weight - Dish\ Weight}{Wet\ Weight - Dish\ Weight} \times 100$$

Table 3-3: Total solids of sample point

Sample Point	Dish Weight	DW + Wet Solids	DW + Dry Solids	TS %	Concentration Ratio
Pre PAA	13.6632	15.5976	14.0003	17.43%	1.00
After Dosing	11.564	13.4974	11.8998	17.37%	1.00
After Evap 2	13.6949	15.4998	14.207	28.37%	0.61
After Evap 1	11.809	13.6978	12.4141	32.04%	0.54
After Evap 3	11.9672	13.8062	12.7477	42.44%	0.41
After Evap 4a	9.1966	10.9148	9.9096	41.50%	0.42
After Evap 4b	7.0515	9.0813	8.0692	50.14%	0.35

The total solids data can then be used to calculate a concentration ratio (see Table 3-3 above). This ratio is calculated by dividing the feed total solids by the sample point total solids (see Equation 3-4 below). This concentration ratio can then be used as correction factor for any analytical results where ion concentrations are being measured.

Equation 3-4: Concentration ratio calculation

$$Concentrat\ ion\ Ratio = \frac{Feed\ Total\ Solids\ \%}{Sample\ Po\,\text{int}\ Total\ Solids\ \%}$$

When a sample is analysed from the evaporator, the results are then multiplied by the corresponding concentration ratio. This gives a normalised result to account for concentration changes caused by evaporation so that it can be more easily compared with sample points in the evaporator.

In the following sections, brief descriptions of the instrumental techniques used in this project are outlined followed by the experimental procedures used to prepare samples to be analysed by the technique in question. Results of these analyses have been subsequently given and discussed.

3.4.1 Issues with Precipitation in Samples of Whey Permeate Examined by the Various Instrumental Techniques

Samples that were taken from the evaporator sample points were observed to settle out a lot of precipitated solids as a result of the solution cooling down. The samples were kept frozen before any analysis was done on them. Once thawed for the first time, to run analysis there was a lot of observed precipitation of lactose. These solids were separated from the solution via filtration before they could be analysed for some tests. Analysis of all the tests had to be carried out over a period of a few days, between which the samples were normally kept frozen for preservation. Upon thawing, for the second time, it was noticed that the already filtered solutions exhibited further precipitation which was observed to have settled out of the sample solution. This precipitate had the potential to give misleading data as adsorption of potential analytes, such as calcium ions and orthophosphates ions onto the settled solids would have had an effect on the final results by giving lower values for these elements.

In order to resolve the issue, the precipitated solid had to be identified. The most obvious possibility was that lactose was dropping out from the solution because of its high concentration. The solid was filtered and dried overnight in a 60°C oven. A KBr disk was made for an infrared (IR) analysis. A reference spectrum of lactose was also run in the IR for comparison. The IR spectra as shown in Figure 3-5, are almost identical to each other, which gives compelling evidence that the solid was lactose that had dropped out due to the decrease in temperature after samples were removed from the evaporators and stored frozen prior to analysis.

Little could be done about this other than filtering at a lower temperature (approximately 10°C in an ice bath) than room temperature thus preventing the solution form being saturated at 25°C.

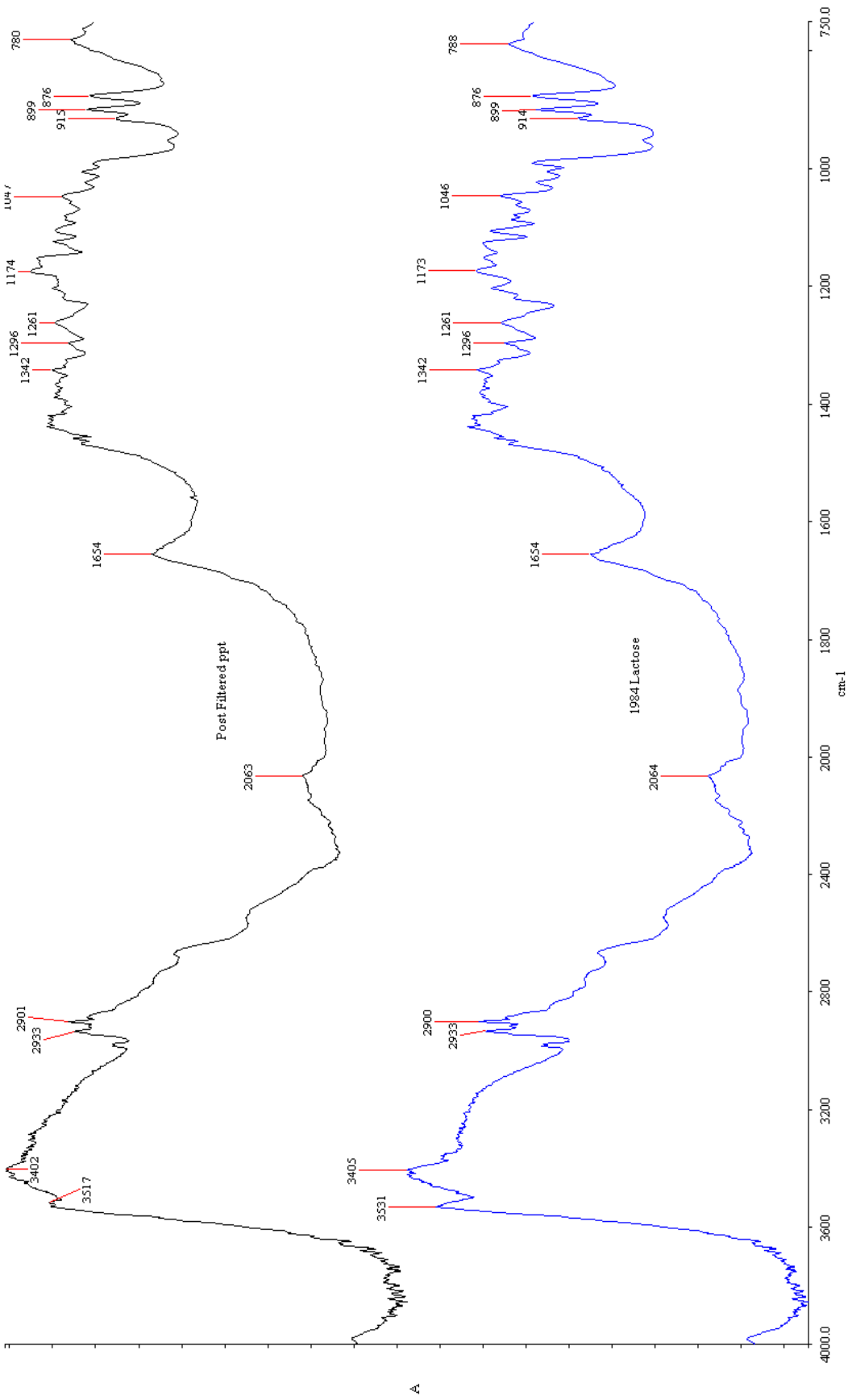


Figure 3-5 Infrared spectra of lactose a) Post-filtered solid from whey permeate samples b) Lactose reference sample.

3.4.2 Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

ICP-MS is a powerful technique for elemental analysis. It is able to detect a wide range of elements down to the parts per billion range. It can be used for analysing solutions or it can be coupled with a laser ablation unit for the elemental analysis of solid samples such as rocks.

3.4.2.1 Theory of an ICP-MS

As the name suggests ICP-MS uses a high temperature plasma torch. This torch reaches temperatures of up to 6000 – 7000 K. At this temperature there is sufficient energy to break down molecules and compounds to their constituent atoms. The molecules are usually in an acidified solution and are introduced into the plasma via a nebuliser which produces a fine mist. This mist is then carried by argon gas into the plasma. The atoms are ionised and focused towards a filter where they are sorted by molecular weight so they are able to be detected (Thomas, 2002).

3.4.2.2 Experimental

Whey permeate samples that were taken from the evaporator were thoroughly mixed to lift the precipitated solids into suspension to create a homogenous sample. It was decided to use an unfiltered sample to include any minerals that may have precipitated out and also those that may have adsorbed onto any lactose present.

Analysis by ICP-MS was conducted on a PerkinElmer SCIEX ICP-MS ELAN DRC II. The software that it used was ELAN v3.3. The ICP-MS is attached to a CETAC ASX-520 autosampler, which could hold a maximum of 240 samples. It featured a SeaSpray nebuliser and a baffled quartz cyclonic spray chamber. A sample flow of 1 mL/min was used with all samples using HNO_3 acidification of 2%. The nebuliser gas flow was set to 0.92 L/min.

3.4.2.3 Results and Discussion

The use of ICP-MS was applied to gain an overall compositional analysis of the whey permeate as it enters the evaporator. It was also used to study the concentration of the selected elements of interest as they travelled through the evaporator. This increase in concentration was then correlated with the concentration ratios mentioned earlier in Table 3-3.

Table 3-4 shows the compositions of selected elements in whey permeate from the Hautapu dairy plant. The results were compared with a study undertaken by Peacock in 2004 (Peacock, 2004), on permeate flows at Hautapu. To make a comparison, the results were corrected for total solids by a normalisation process where the ICP-MS measured concentrations were divided by the total solids expected. This normalisation process was applied to both sets of results. This gave a composition at 1% w/w total solids. With the same solids percentage, elemental comparison could be made.

Table 3-4: Normalised permeate compositions at Hautapu compared with Peacock (Peacock, 2004)

Element	ICP-MS mg/Kg	Peacock 2004 mg/Kg
Sodium	47.66	62.58
Magnesium	11.88	13.23
Phosphorus	67.98	2.44 (phosphate)
Potassium	237.44	249.0
Calcium	37.95	65.84

Relative levels of each element for each experiment are similar but Peacock's results are higher than those obtained from the ICP-MS. This could come down to many factors including seasonal variations and difference in instrumentation. There is a discrepancy in the levels of phosphorus. Peacock has mentioned that she measured phosphate, which is assuming to be orthophosphate, but 2.44 mg/Kg is very low. The source of this result could not be obtained. Comparison with dissolved reactive phosphate obtained in this study could not be used as a comparison with Peacock's as these too gave unreliable results, which suggests that measuring orthophosphate in a whey permeate medium can be difficult.

It is not stated how Peacock obtained her samples but comparing the relative levels of each element, with the exception of phosphate, indicates that the composition is similar to that obtained in this project. A more reliable explanation for the higher results from Peacock is the time in which that sample was taken. It is known that seasonal variations can have an effect on the composition of milk (Ozrenk & Inci, 2008). This can include the type of feed, whether the cows are eating pasture or are on supplementary feeding.

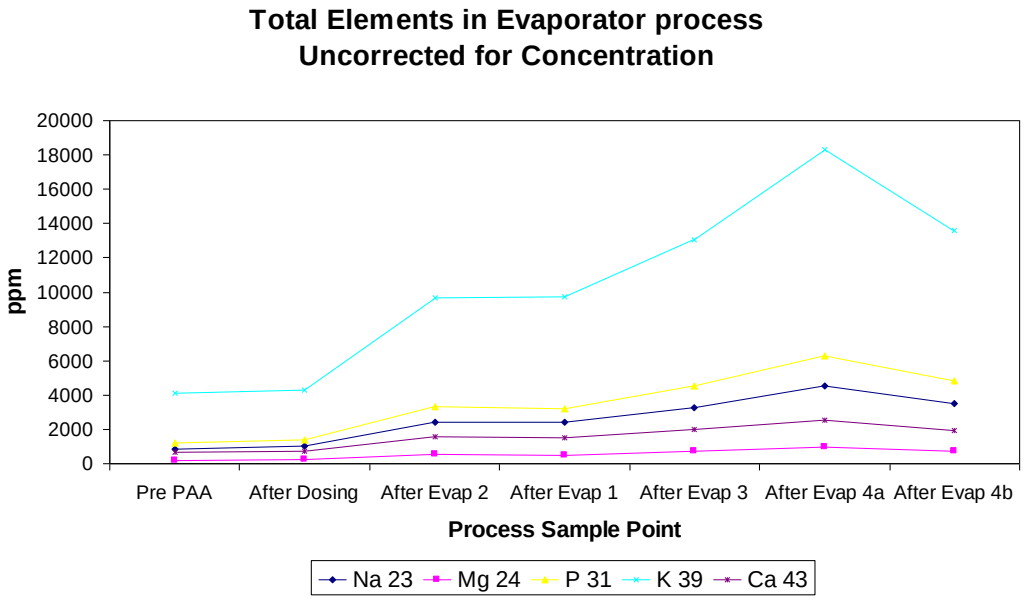


Figure 3-6: Total elemental analysis of whey permeate through the evaporator (uncorrected for concentration)

Figure 3-6 shows the uncorrected rise in elemental concentrations (as measured by ICP-MS) of the permeate at various sampling points through the evaporation process. It hence shows how the permeate changes in concentration as it travels through the Holvrieka evaporator. The overall trend is for an increase in the elemental concentrations but there are also some fluctuations at the 3rd and 7th sampling points. For the higher solids samples, for example "After Evap 4b", there was difficulty in getting an accurate volume because there was an increase in precipitated solids that may have contributed to errors in obtaining an accurate volume. As the density of the solution samples increased, along with the concentration of elements, the lactose concentration also increases. This

reduction of water from the bulk solution causes the lactose to become supersaturated and precipitate out of solution.

When the samples are cooled the lactose precipitates causing lumping to occur. It was deemed that the precipitated lactose was important for analysis as some of the elements would have adsorbed onto the surface of the lactose crystals. Getting an accurate volume of a lactose solution at 50% total solids proved difficult as the viscosity was high and there was a lot of precipitated solids. This could account for the fact that there was a discrepancy in the data for the last sample point in the evaporator.

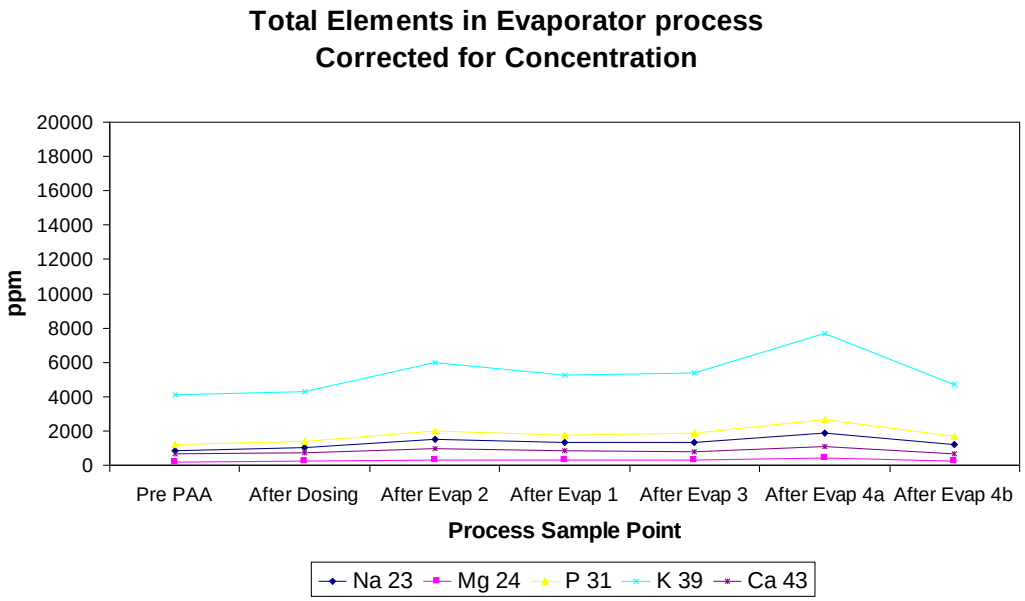


Figure 3-7: Total elemental analysis of whey permeate through the evaporator (corrected for concentration)

Figure 3-7 show the total concentration of elements after the concentration ratio, from Table 3-3, has been applied. The ICP-MS results show a more normalised trend where the effect of concentration is removed. There still seems to be a small rise in concentration through the evaporator but the effect has dramatically been reduced. The fluctuations, especially in the last calandria, show the difficulty of gaining accurate results for tracking the fate of PAA through the evaporator for reasons relating to high amount of precipitated solids.

Due to the fluctuations between sample points and the low levels in which PAA was being dosed into the evaporator, it was decided from the total elemental analysis to abandon efforts in tracking PAA though the Holvrieka and focus on tracking PAA in a more controlled laboratory setting. It was hoped that the fate of PAA could be followed through the evaporator but the low level of dosing and the fluctuations in results means that the detection of PAA would lay within the margin of error. The difficulty of detecting PAA as phosphorus levels were amplified by the nature of the whey permeate at higher densities and precipitated solids.

3.4.3 Calcium Ion-specific Electrode (Ca ISE)

This was used with the intention of detecting the free calcium ion level in whey permeate samples. It was proposed that the free calcium level could be correlated against the ICP-MS results to give an indication on the amount of bound calcium ions. "Bound" calcium ion is that which is notionally sequestered by the PAA as per the current thinking in the industry. However, as will be described later in this section, the use of this electrode encountered many practical problems caused by the compositional complexity of the permeate samples, which resulted in poor inter-instrument comparison of results. Ca ISE results were compared with ICP-MS results shown earlier but discrepancies between the two meant that relative concentrations could not be compared with any certainty.

3.4.3.1 Theory of Operation of the Ca ISE

In metals an electric current is carried by electrons but in solution the electric current is carried by ions. A Ca-ISE has a liquid-membrane that develops a potential across the interface between the solution containing the analyte and a liquid-ion exchanger that selectively bonds with the analyte ion. A calcium ion electrode consists of a conducting membrane that selectively binds to calcium ions. It also has an internal solution containing a fixed concentration of calcium chloride and a silver electrode that is coated with silver chloride to form an internal reference electrode. The potential that is generated in a solution is

proportional to the concentration of calcium ions and is dictated by the Nernst equation (Equation 3-5).

Equation 3-5: Nernst equation

$$E = E^{o} + \frac{2.303RT}{nF}\log(a)$$

Where E is the total potential (in mV) developed between the solution and reference electrodes, E° is a constant being the standard electrode potential, which is characteristic of the particular Ca-ISE, hence the need for daily calibration, R is the Gas Constant (8.314 joules/degree/mole), T is the Absolute Temperature in Kelvin, n is the number of electrons transferred in the electrochemical reaction taking place, which is 2 for calcium, F is the Faraday Constant (96,500 coulombs per mole) and log(a) equals the logarithm of the activity of the measured ion. Activity is equal to concentration of the calcium ion multiplied by the activity coefficient. Note that the activity is equivalent to the concentration in very low ionic strength solutions because the activity coefficient tends towards a value of 1. In higher ionic strength solutions, however activities become more important.

Since the ionic strength is relatively high in whey permeate (~ 0.1 mol L^{-1}) it is important to know what the ionic strength is. Ionic strength between samples needs to be constant if meaningful measurements are to be taken.

3.4.3.2 Experimental

Calcium ion determination was carried out with a Radiometer ISE25Ca Calcium Electrode (Figure 3-8). The electrode was capable of detecting calcium ions in the concentration range of 2 x 10^{-6} M to 1 M, with a typical detection limit of 4 x 10^{-6} M.

Calibration was carried out by using a 0.001 mol L^{1-} Ca^{2+} stock solution. 0.1001 g $CaCO_3$ was added to a 1 L volumetric flask with approximately 500 mL distilled water. To this 2 mL of 1 mol L^{1-} HCl was added to dissolve all of the $CaCO_3$. 24.25 mL of KCl was added to increase the ionic strength to give an overall ionic

concentration of 0.1 mol L^{1-}. Dilute NaOH, with a pH of approximately 0.1 mol L^{-1} was added where required to neutralise the pH. The calculation of a stock solution of 0.001 mol L^{-1} Ca^{2+} with an ionic strength of 0.1 mol L^{-1} is given in Appendix B.

A series of calcium concentrations was used to construct a calibration curve. 0.001, 0.00075, 0.0005, 0.00025 and 0.0001 mol L^{1-} calcium ion solutions were made by adding 0, 187.5, 125, 62.5 and 25 mL of stock solution into a 250 mL volumetric flask. The volumetric flask was made up to the mark with 0.1 mol L^{1-} KCl to preserve the ionic strength. Since the ionic strength can be variable in milk and hence in whey permeate, it was important to have a constant ionic strength of 0.1 mol L^{-1}.

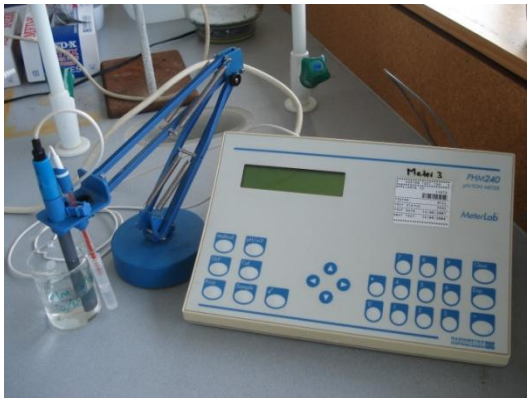


Figure 3-8: Photograph of calcium ion electrode and meter

3.4.3.3 Results and Discussion

When taking measurements using the Ca-ISE in whey permeate samples equilibration took a long time to achieve. Usually a period of up to two minutes or more was needed to get a stable reading. This was more prevalent with the viscous permeate samples of higher solids. It was found that despite the issues with reading stabilisation, measurements did relate well to one another but as mentioned earlier in this section there were discrepancies when the Ca ISE data were compared with ICP-MS data. This will be discussed further in this chapter.

Figure 3-9 shows the results of an experiment where an attempt was made to get the first fouling rig to foul. Four litres of whey permeate was heated to 75°C in a water bath and the rotating cylinder was submerged into the solution. As well as attempting to cause fouling onto the rig, samples were taken over a 16 minute period and analysed for free calcium ions and total calcium by ICP-MS. The data shows that the two methods that were used, Ca-ISE and ICP-MS, could not be compared as the total calcium data obtained through ICP-MS measurements worked out to be less than the levels of ionic calcium measured by the Ca ISE electrode.

To measure each sample a sub sample of 100 mL was taken and cooled to room temperature. The graph below shows that there is no decrease in the amount of ionic calcium. It was hypothesised that if fouling was taking place onto the stainless steel then there would be a decrease in both the total calcium and ionic calcium in the solution.

As no fouling was observed, even after rotating in the solution for eight hours, it was not surprising that the total calcium did not decrease. What was unexpected was that the ionic calcium also stayed constant throughout the experiment. It was expected that if the solution was heated, then over time calcium would precipitate lowering the amount of calcium ions.

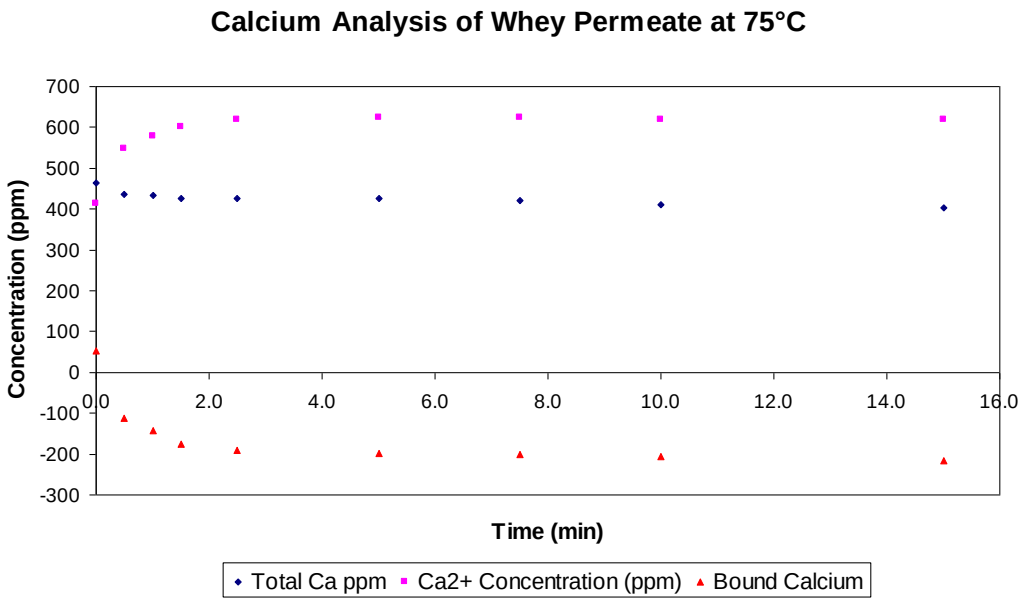


Figure 3-9: Comparison between free calcium ions obtained by Ca-ISE and total calcium obtained by ICP-MS

The "Bound Calcium" in Figure 3-9 was supposed to signify the calcium that was not in an ionic form but as the graph illustrates there was obviously a significant error involved in inter-instrumental interpretation. Because the ICP-MS results were quite similar with Peacock's results, with the exception of phosphate, it was believed that the inaccuracy was in the Ca-ISE measurements. There was trouble in finding a suitable ionic strength for the whey permeate samples because of the unknown concentrations of all of the ionic species present.

Earlier studies involving the use of calcium electrodes in measurements on dairy-sourced samples also reported problems. For example, a study carried out by Lin *et. al.* (Lin *et al.*, 2006) demonstrated the difficulty of analysing free calcium in milk samples. They concluded that there were two main difficulties in using a Ca-ISE similar to the one used in this experiment. The first was that the equilibration time could take up to 10 minutes in milk samples after being used on standards. This led to a shifted and unstable baseline. The second was that when the electrode was flushed between samples with distilled water, it sometimes altered the baseline reading for the membrane potential. They concluded that this type of Ca-ISE was not reliable for rapid measurement for ionic calcium in milk.

This could also be applied to whey permeate as they are both complex systems where matrix effects can cause the inaccuracy observed in the concentration.

Another issue with the use of Ca-ISE electrodes is that they may also not be so "specific" to calcium ion. There are other ions that can interfere with its reading, such as Pb^{2+}, Fe^{2+}, Ni^{2+} and Hg^{2+} and most relevantly for whey permeates, Mg^{2+} ion. It is presumed that these are not in any significant levels to have an effect and that more fundamental problems were probably to blame for the results. The most likely explanation for the interference in readings is the amount of precipitated solids which might have fouled the electrode. They could also have had an effect on the ability of ions to carry an electrical current in the system by causing a decrease in mobility of ions in the matrix. Also some matrix effects can cause changes to the overall ionic strength such as citrates which are known to bind calcium (Odagiru & Nickersion, 1964).

One of the original aims of using Ca ISE electrodes to measure free calcium ion levels in the permeate was to find a way of gauging to what extent PAA binds free calcium ion in the permeate as it is the free ion which must react with orthophosphate ion to produce the calcium phosphate fouling. Hence, to see the effects of PAA on calcium ion levels in the whey permeate an experiment was conducted that involved two lots of four litre whey permeate samples. Both had the fouling rig submerged in the solutions but only one was dosed with PAA at levels similar to that seen at Hautapu Dairy Factory. The experiment was carried out over a period of 15 minutes to see if there was any effect on the amount of fouling on the rig. The results are displayed in Figure 3-10.

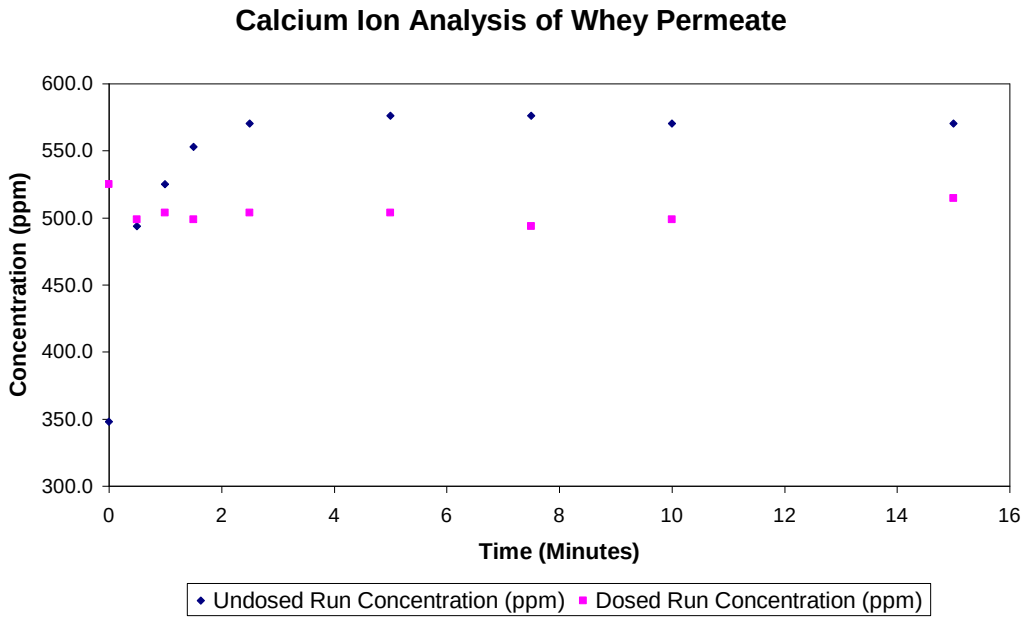


Figure 3-10: Calcium ion analysis of whey permeate dosed and undosed with PAA

Although, the absolute numbers representing the free calcium ion concentration measured by the Ca ISE did not appear to be realistic concentration values, it was interesting to note that it did reflect an expected trend for Ca ion concentration when PAA was present in whey permeate. Figure 3-10 represents the free calcium concentrations measured by a Ca ISE where the free calcium was measured on two separate samples over a period of 15 minutes. One was a control sample (the undosed run) while the other was a dosed run with 0.4% PAA. The undosed run shows a steady increase in concentration before it steadies out at around the 3 minute mark. This could be due to the effects described above where the electrode needs time to equilibrate.

The sample that was dosed with PAA in Figure 3-10 showed a noticeable decrease in free calcium ion concentration. If the conditions for the correct measurement of absolute value of free calcium ion concentration by the Ca-ISE had been correctly achieved, this would mean that in the presence of PAA, the free calcium ion concentrations would be lower as expected because they were being chelated by PAA in a similar manner to EDTA as a complexing agent. It will be later explained that calcium ions form a precipitate with PAA but due the lack of transparency of whey permeate with suspended solids such as lactose, this

precipitate was not observed at this part of the project. It will be discussed in this chapter that the precipitation can be seen visually however only if the permeate is filtered beforehand.

3.4.4 Dissolved Reactive Phosphate (DRP)

This technique was chosen as a means of differentiating between orthophosphate and polyphosphate in solution. In initial discussions on the measurement strategies for trying to follow PAA's fate through the whey permeate stream, this method coupled with the total P measurement method by ICP-MS was reasoned to provide some differentiation between PAA and orthophosphate in solution. The DRP measurement technique is a colorimetric technique which is conventionally used to test the orthophosphate levels in water systems. For use in determining calcium phosphate fouling, Amjad (Amjad, 1998) discusses his analysis for determining orthophosphate levels in water systems by a spectrophotometric method. It was assumed that dissolved reactive phosphate (DRP) was determined in a similar way. Applying a method used on water systems and that which was used by Amjad, it was assumed that this method could be successfully transposed to orthophosphate determination in whey permeate.

3.4.4.1 Theory of Detecting Orthophosphate via the DRP Method

In a solution containing small amounts of orthophosphate, up to 10 mg/L, ammonium molybdate reacts under acidic conditions to form a heteropoly acid, molybdophosphoric acid. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The colour of the yellow acid is proportional to the concentration of the orthophosphate ion in solution.

3.4.4.2 Experimental

For the determination of orthophosphate a standard stock solution of 219.5 mg anhydrous KH_2PO_4 was dissolved in a 1 L volumetric flask with distilled water and made up to the mark. This gave a final concentration which related to 1 mL of solution being equal to 50 µg PO_4^{3-}.

To construct the calibration curve, a series of standards from the stock solution corresponding to 20, 15, 10, 5 and 2.5 ppm of PO_4^{3-} were made. This was done by following the procedure below with the sample amounts being 14, 10.5, 7, 3.5 and 1.75 mL of stock solution respectively.

Whey permeate samples were diluted 500 times in distilled water to get a final perceived orthophosphate concentration within the range of the experiment, between 2-10 ppm. This was taken from the EPA method 4500-P C, Vanadomolybdophosphoric Acid Colourimetric Method (Eaton *et al.*, 2005). For the reagent solution two reagents, Solution A and Solution B were first made. Solution A was made by dissolving 25 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 300 mL of distilled water. Solution B was made by dissolving 1.25 g ammonium metavanadate, NH_4VO_3, in 300 mL of distilled hot water (80°C). The solution was left to cool and then another 330 mL of concentrated HCl added. The solution was then cooled down further to room temperature upon which Solution A was poured into Solution B and mixed. The mixed solutions were then made up to the mark of a 1 L volumetric flask.

Measurements were taken by placing 35 mL or less of the diluted sample (the amount of sample does not have to be 35 mL but the exact volume must to be known), containing 0.05 to 1.0 mg of orthophosphate, in a 50 mL volumetric flask. To this 10 mL of the vanadate-molybdate reagent was added and the solution was made up to the 50 mL mark with distilled water. A blank was prepared in which 35 mL of distilled water is substituted for the sample. After 10 min or more the absorbance of the sample was measured versus the blank at a wavelength of 420 nm. The colour was stable for days and its intensity was unaffected by variation in the room temperature. Once the absorbance was recorded and correlated with the calibration curve then the final concentration could be found by using Equation 3-6.

Equation 3-6: Calculation of concentration in DRP sample

$$Sample\ Concentrat\ ion\ (ppm) = \frac{mg\ P\ (in\ 50\ mL\ \ final\ volume) \times 1000}{mL\ Sample}$$

3.4.4.3 Results and Discussion for DRP Measurements.

As stated above, it was hypothesised that DRP measurements could be used to distinguish between orthophosphate in the whey permeate and the polyphosphate, a non-orthophosphate species hence not detectable by the DRP method, of PAA. Unfortunately, there were also problems encountered with the use of this analytical technique on whey permeate samples and discrepancies noted when it was compared with the ICP-MS data, similar to those noted when comparison of ICP-MS and Ca-ISE derived data were made.

As part of a preliminary experiment to detect PAA through the evaporator, DRP measurements were taken at each calandria of the evaporator. Figure 3-11 shows the steady rise in orthophosphate levels as the permeate is concentrated (the graph is not compensated for concentration). This is due to the increase in solids as mentioned earlier as the permeate is evaporated. This graph was indicative of the error related to this technique and that of the ICP-MS analysis. Comparing these results with those given in Figure 3-6, it shows that the amount of orthophosphate is higher than that of the total phosphorus. This effect is also further discussed and reiterated again later in this section.

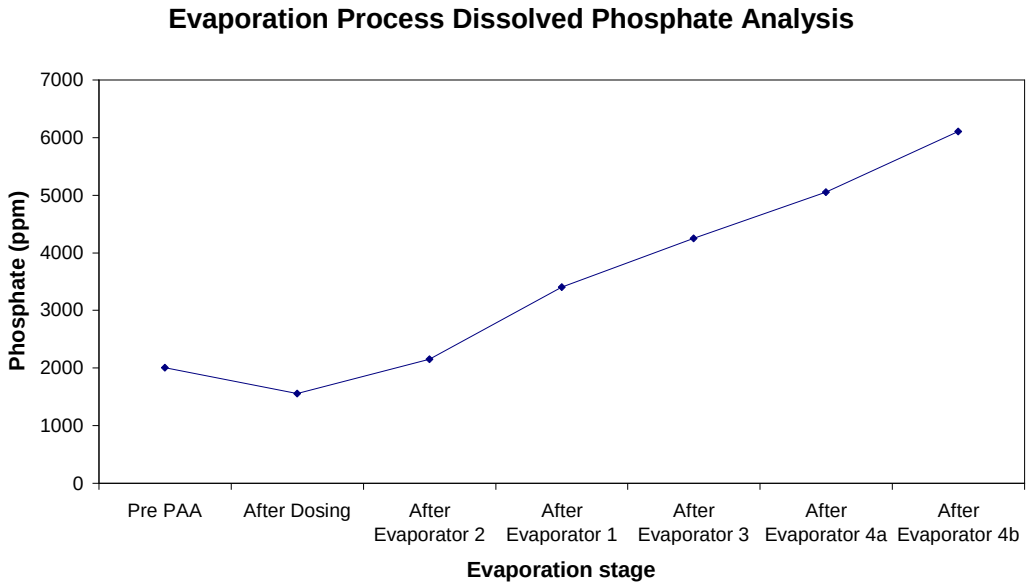


Figure 3-11: DRP measurements of whey permeate through the evaporator uncorrected for total solids

To get a direct analysis of DRP and total phosphorus from ICP-MS an experiment was set up that was explained earlier when comparing free calcium ions with total calcium. Heating whey permeate and taking samples over a 15 minute duration, during a fouling rig experiment, gave similar results to the calcium measurements. The results of the phosphate analysis are given in Figure 3-12.

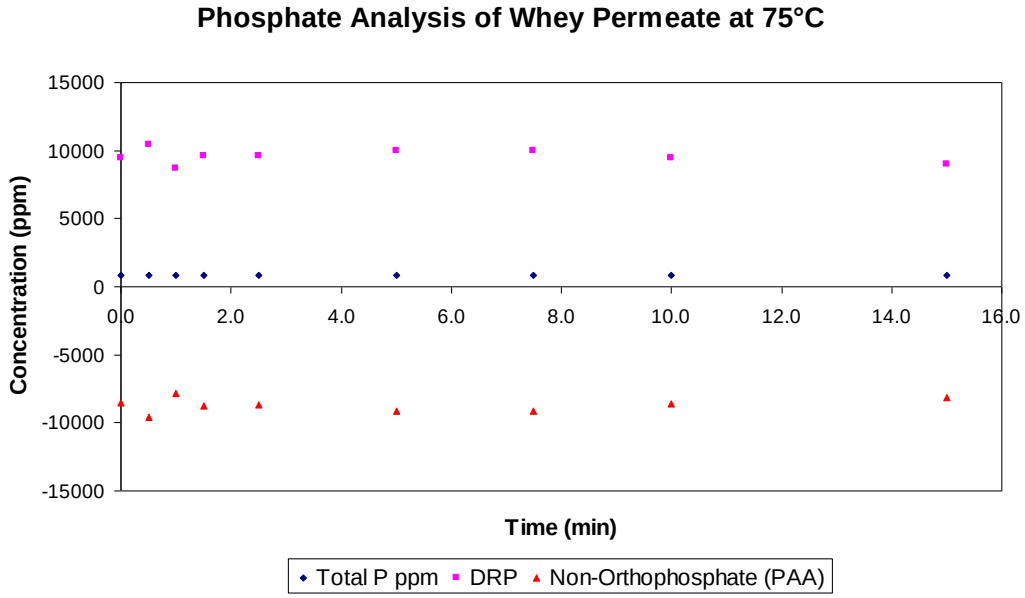


Figure 3-12: Comparison between DRP results and ICP-MS

Figure 3-12 again shows the poor inter-instrumental comparison of results, similar to the calcium electrode results. DRP analysis gave much higher results than the total phosphorus which is theoretically impossible. DRP cannot exceed the total level phosphorus because DRP must be a subset of the total phosphorus. The rest of the total P "signal" from ICP- MS measurements can be attributed to other forms of phosphorus such as in proteins or polyphosphates or even as lactose phosphates. The discrepancies may also arise from matrix effects the whey permeate acting upon the DRP experiment. It was also noticed that on some whey permeate samples a fine solid appeared when it was mixed with the colouring agent. This precipitate was very hard to isolate and was ultimately unidentified. It proved difficult to remove the very fine particulate matter via filtration even through a .45 micron filter, so UV measurements were carefully taken after sedimentation had occurred by carefully pipetting the surfactant into the UV cell. Any suspended matter that was still prevalent would have a dramatic affect on the absorbance signal. The suspended matter would give a falsely high reading as it would scatter light that would otherwise reach the detector. Although no suspended matter could be seen with the naked eye the possibility that some particulate matter was still present, possibly in colloidal form, cannot be ruled out. It is recommended that centrifuging the fine precipitate out instead of gravitational settling could provide a more accurate reading in the future.

Since the DRP test was reasoned to be able to differentiate between orthophosphate and polyphosphate in solution, a simple experiment was set up to test the heat stability of PAA. It was thought that PAA was not effective in the later parts of the evaporator, where fouling is usually heaviest, due to the possibility of degradation. So an experiment was designed to take samples of PAA in an aqueous solution at defined intervals as the temperature was increased.

Five grams of PAA was dissolved in 250 mL of water and then heated until boiling; a sample was withdrawn at 10°C intervals and a DRP measurement taken. The results are shown in Figure 3-13. The findings were not that surprising at lower temperatures given the polyphosphate molecules, making up the PAA, are resistant to degradation. Although there does seem to be some level of

orthophosphate present which can be expected from an industrial grade product. Any added orthophosphate to the whey permeate system will only hinder PAA's ability to act as an inhibitor. When however the sample containing PAA was left to boil for 30 minutes, the DRP measurements indicate that the orthophosphate level rose significantly giving evidence that the PAA or polyphosphate, was breaking down to orthophosphate and hence becoming ineffective as an inhibitor and more of a fouling promoter given the generation of free orthophosphate into the system.

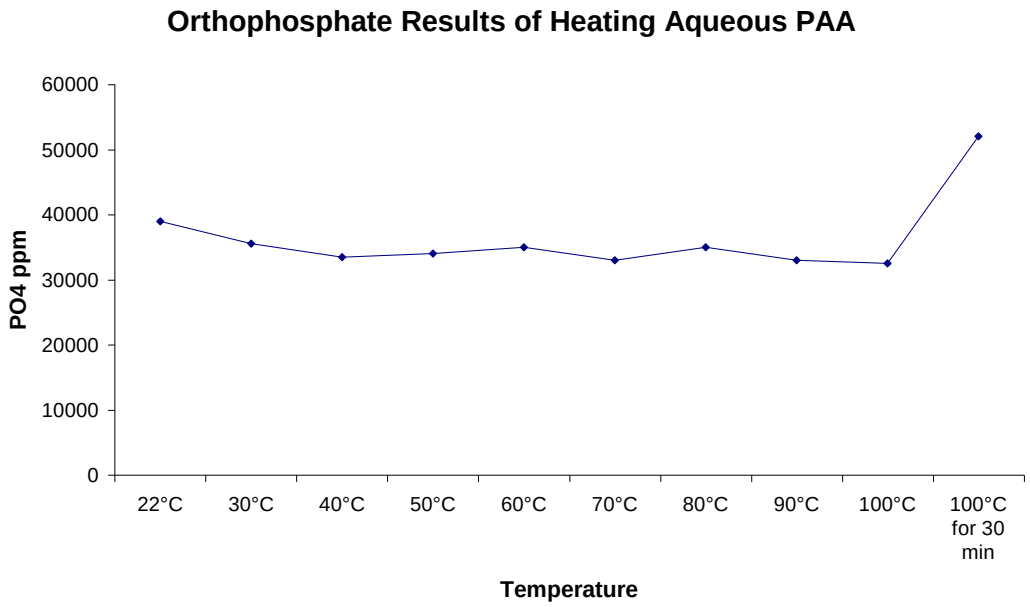


Figure 3-13: Effects of temperature of PAA using DRP analysis

This result is backed up by Rashchi and Finch who discuss the conditions in which polyphosphates can hydrolyse to orthophosphate. Polyphosphate hydrolysis is strongly acid-catalysed and like all condensed phosphates, they can eventually be converted to orthophosphates by boiling (Rashchi & Finch, 2000).

This supports the evidence that is seen and also argues that PAA is hydrolysing in whey permeate, which is slightly acidic and can have a pH as low as 4.7. These acidic conditions coupled with the boiling of the permeate at 70°C under vacuum supports the claim that PAA is degrading in the evaporator but because of the low

dosage levels and the difficulty of direct measurement this is difficult to confirm conclusively.

Because the DRP only tests for orthophosphate ion (PO_4^{3-}) it is not clear from the results whether or not the PAA is breaking down before the final reading, into somewhat smaller chain length polyphosphates than the original chain lengths present, for example, whether it is breaking in the middle of the chain into smaller fragments or hydrolysing from each end gradually reducing the chain length. Also since the conditions in the evaporator are a lot harsher because of the fact that the system is operating under a vacuum, the permeate is much more highly volatile at 70° C, which could mean that the PAA is possibly decomposing through part of its journey in the evaporator. PAA may not necessarily have to degrade to orthophosphate for it to become ineffective, the reduction of chain length may also have a decrease in sequestering ability. If however PAA is degrading to orthophosphate then this is only going to contribute to the degree of fouling seen in the later calandrias of the evaporator. As an aside to this experiment, a small amount (~5g) of calcium chloride was added to the aqueous PAA solution. Surprisingly a white precipitate formed which was unexpected. This precipitation shed new light on how PAA could interact with calcium ions to prevent fouling. Further investigation of this is discussed in Chapter 4.

3.5 Overall Discussion and Conclusion of Results

To directly measure fouling in the evaporator an initial approach was taken that involved taking composite samples from each calandria and testing them to determine the rate of fouling as permeate was passed through the system. To do this, a number of assumptions were made in relation to the levels of PAA that were anticipated to be detected.

For the direct measurement of PAA in the evaporator, it was assumed that the remaining phosphate that was not an orthophosphate ion was composed of PAA. This assumption was justified on the basis that any phosphate that is in whey, is either in the form of proteins or in solution as orthophosphate. Since the whey is

ultra-filtrated to remove the bulk of the proteins, the remaining phosphate in the feed stream leading into the evaporator should be predominantly orthophosphate. Therefore the total phosphate concentration minus the DRP concentration was hoped to give a PAA concentration but in practice, the difficulty of analysing the more highly concentrated permeate samples and the high inter-instrumental error from the ICP-MS and the Vanadomolybdophosphoric Acid Colourimetric Method gave poor results. Reflecting on the results, this proposed model may have been an over simplification of a complex system as it is known that UF-membranes can wear out and allow some protein to pass through. The data was poor because of unrealistic results and how the orthophosphate levels showed to be falsely higher than the total amount of phosphorus present.

There were many complications that arose from this part or the project that ultimately led to the changing of the overall goals of this project. Inter-method comparisons and lack of mineral fouling on the laboratory rigs were the main sources at fault for this part of the project not coming to fruition. The difficulties of this stint of work, as described below, did however lead on into the investigation of PAA's interaction with calcium ions. As it was discovered, when the system was simplified to test for the heat stability of PAA, that PAA precipitates out of a calcium solution.

Direct measurements of whey permeate from the evaporator failed to turn out any reliable results because of the low levels of PAA that are dosed and the fluctuation in the concentration ratios at higher solids. ICP-MS analysis of total ions, shown in Figure 3-6 and Figure 3-7, illustrates the fluctuations involved in the analysis of the higher solid samples. When the concentration ratios are applied from Table 3-3, the results become more relative to each other but still had a high degree of fluctuation and hence error associated with them to be reliable.

As mentioned earlier in this chapter, matrix effects, due to the highly complex ionic environment of the permeate, were a big problem for analysing whey permeate samples. Other components such as citrate and lactic acid contribute to the complexity. These matrix interferences extended to the analysis of DRP and calcium ions. As mentioned earlier in this chapter, when testing for DRP a very

fine precipitate was seen that was difficult to filter. DRP testing gave trends that appeared realistic from expectations but the data was unreliable and could not be compared to the ICP-MS. Calcium ion concentration was also prone to matrix effects and to ionic strength variations. This was witnessed when Ca-ISE data was compared to ICP-MS data. Both the DRP and calcium ion analysis studies gave indicative trends which agreed with what was expected notionally in the system but the results were unreliable for quantitative analysis.

Chapter 4: Identification and Characterisation of PAA

The project goals outlined in Chapter 1 changed to reflect the events brought about by the difficulty of obtaining reliable results from initial investigations. The project goals changed in response to a need to gain more understanding about the characterisation of PAA and more specifically what the chemistry between PAA and calcium ions was in an aqueous environment, with the desire of firstly tracking its fate in the permeate streams after dosing and secondly optimising its use in Hautapu Dairy Factory. In the previous chapter, it was shown that creating mineral fouling in the laboratory scale rig was difficult. This was coupled with the uncertainty about the reliability of results caused by matrix interferences in the methods chosen for analysis of whey permeate. A new line of enquiry was hence needed. It was found fortuitously that when a simple addition of PAA to a solution of calcium chloride was carried out, an insoluble white precipitate was produced. This simple observation provided an interesting and possibly profound revelation into how PAA might function in the whey permeate stream and hence the project's goals changed tack to further investigate this observation and its implications. The bulk of the study was thus centred about the PAA-Ca precipitate that was produced and whether this was affecting the efficacy of PAA as an antifouling agent in the whey permeates.

This chapter, therefore, focuses on the identification and characterisation of PAA using various instrumental techniques of which a brief description is given for each. It also provides in greater detail, different variables that affect the formation of the PAA-Ca precipitate. The interaction of PAA with calcium ions on a bench scale (under some of the selected conditions that are similar to whey permeate) gave a clearer representation of how PAA worked in the Holvrieka evaporator at Hautapu.

The first aspect of the identification and characterisation of PAA was to focus on a dry sample of PAA from the supplier, Orica Chemnet Limited. PAA usually arrives on site at Hautapu in liquid form where it has already been previously

dissolved to 40% solids with a density of 1.28 g/L. A solid sample of PAA was obtained, in the form of a white odourless powder, for testing. This was used as the basis of scientifically identifying what PAA was in terms of a specific compound given the previous knowledge, which was judged inadequate for scientific purposes, that PAA was a "polyphosphate processing aid".

All previous knowledge of PAA up to this point was that it was a form of polyphosphate without knowing what the specific compound was. However for the purposes of a systematic chemical investigation, this description is inadequate. It was not known whether PAA was a tri-phosphate or if it had a larger degree of polymerisation. To help identify what PAA was chemically, other similar polyphosphate-type compounds offered commercially were investigated. These included Sodium Polyphosphate (SPP) and Sodium Hexametaphosphate (SHMP). These two reference chemicals were used as a comparison to help identify the composition of PAA.

4.1 Introduction

To investigate further how PAA precipitates out of an aqueous calcium solution, it was decided to investigate this phenomenon in greater detail. It was anticipated that this investigation would lead to a better understanding of how PAA works in whey permeate and its role as an anti-fouling agent. The realisation that polyphosphates can precipitate out in high hardness waters has been well known to the desalination industry. High hardness in water is mainly due to calcium, which results in the permanent precipitation of calcium polyphosphates when PAA is added as an antifouling agent. Amjad (Amjad *et al.*, 2003) classed this phenomenon, at which the point where a precipitate permanently appears in solution after adding a precipitating agent, as 'calcium tolerance'. The reference of 'calcium tolerance' in this scene is usually restricted to the desalination and water industries but the term has also been used for the purpose of this study.

As stated above, calcium tolerance is the ability of a compound or additive to stay soluble when calcium ions, that can precipitate out the dissolved compound in

question, are also present. A compound with low calcium tolerance will precipitate out as a calcium salt from a solution where low calcium concentrations are present. A compound with a very high calcium tolerance however, will tend to stay soluble in high calcium concentration solutions and hence work more efficiently as a scale inhibitor in high hardness waters.

Polyphosphates are used to reduce scale build up in water systems that can accumulate calcium scale. Recirculating water systems tend to increase in their calcium hardness as vapour (pure steam) is steadily lost and new water, which contains small amounts of dissolved minerals such as calcium, is brought into the system. As the level is maintained by the incoming water with dissolved salts, an increasing amount of minerals are 'trapped' in the system, thus gradually increasing the hardness of the recirculating water over time where eventually deposits will form. An analogy of this is the scum that can build up in a water distillation system.

In the case of whey permeate, the calcium ion levels in solution are much greater than those typically observed in potable water systems. This would suggest that the PAA concentration would exceed the calcium tolerance level in the whey permeate. Indeed this is what is seen when feed stream whey permeate is filtered and the recommended evaporator dosing rate of PAA is added. This has previously been seen in a Fonterra study carried out by one of the plant supervisors, (Burgess, 2006), at Spreyton Tasmania Australia, but was classed as calcium orthophosphate-associated fouling rather than calcium polyphosphate. As the precipitate was not chemically identified, a full characterisation of the white solid cannot be made.

In the Tasmanian study, filtered whey permeate was dosed with the recommended amount of PAA and then heated to 80°C before the precipitate was left to settle. It is not clear whether the precipitate formed upon dosing and prior to heating or whether heating was necessary. The precipitation experiment is displayed in Figure 4-1. There was a range of PAA levels that were added to separate whey permeate samples. The sample with the recommended dosing rate showed the formation of a white precipitate. The permeate sample with a PAA level well

above that recommended, showed on the other hand, no visible precipitate after heating suggesting that higher PAA levels were best. The fundamental problem with this study, however, was that there was no control (heated) permeate sample without PAA added. This would have shown more conclusively that PAA interaction with the permeate on heating was causing the formation of the precipitate and not 'fouling minerals' like calcium-based materials.

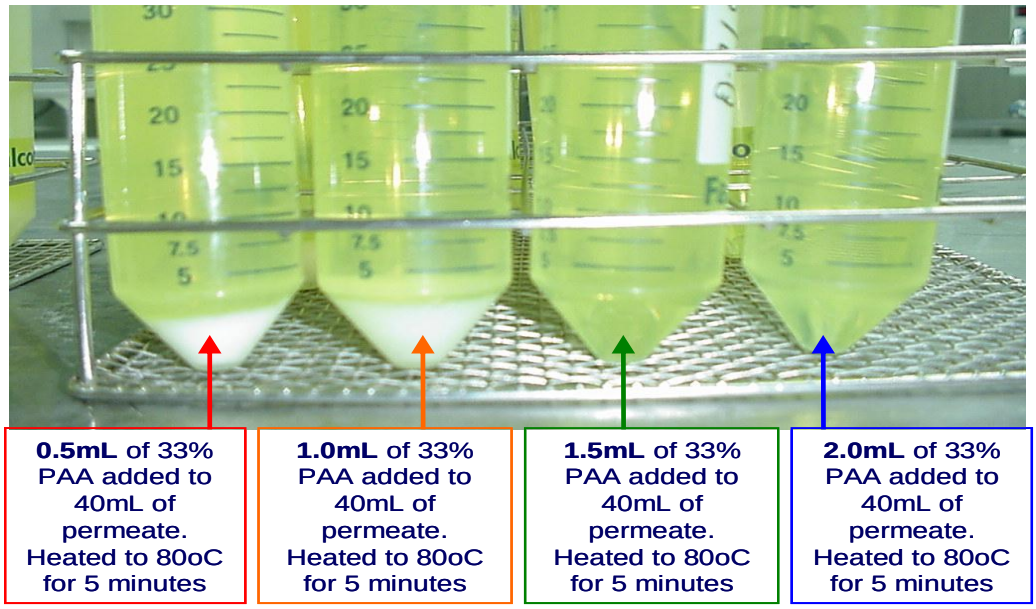


Figure 4-1: Process Aid "A" optimisation project. George Burgess – Spreyton, Feb 2004

4.2 Instrumental Techniques used to Study Polyphosphate Salts

4.2.1 Scanning Electron Microscopy and Energy Dispersive X-ray Analysis (SEM/EDX)

Scanning Electron Microscope was used as a qualitative analytical tool to aid in the chemical identification of PAA and its calcium adducts. It is a powerful technique that can be used for elemental analysis and also can look at a substance's 3-d morphological characteristics in much higher magnification than can be seen with the naked eye or an optical microscope.

4.2.1.1 Theory of a SEM

In a scanning electron microscope (SEM) instrument, images are formed by the collection and amplification of electrons backscattered or emitted from the surface of a bulk specimen. Scanning electron microscopy is comparable to the use of a light microscope but instead of photons being used to produce an image on the eye (as a result of looking through the eyepiece of a light microscope), a stream of electrons is used to produce an image on a cathode screen. This can be represented by Abbé's equation, for a perfect optical system.

Equation 4-1: Resolution equation for SEM

$$d = \frac{0.612\,\lambda}{n \sin \sigma}$$

The resolution of an SEM (d) is directly proportional to the wavelength of the electrons (λ), represented by Equation 4-1. In this equation, n is the refractive index, which is 1 under the vacuum of an SEM and σ is half the angle of the cone of light from specimen accepted by the object. Since electrons have a shorter wavelength than visible light, they produce a higher resolving ability so allowing a greater degree of magnification. For an image to be produced by the instrument the sample needs to be placed under vacuum and the electrons are focused onto the sample by electromagnets. The image is then constructed point by point by the detection of backscattered electrons and secondary electrons. Backscattering electrons are of similar energy to the incident beam and are produced by the interaction with the nucleus of the sample atoms. Secondary electrons are lower in energy and are produced from the interaction of the electron beam with the conduction band electrons in the sample (Zhou & Wang, 2007). The image is compiled in the same way a black and white television works. Surfaces that reflect more electrons give a brighter image on the screen.

Energy dispersive X-ray analysis is the analytical technique associated with SEM instruments. It is based on the fact that the electron beam, with a sufficient amount of energy, removes the inner shell electrons from atoms in the sample. The atoms are then excited or ionised with excess energy. The removed electrons

are replaced by electrons from a range of outer shells, depending on the atomic number. This displacement results in the release of energy in the form of X-rays (Kα), which can then be counted. The count rate on an area of the sample is measured for specific elements which can be compared to the count rate of a standard of pure element or pure alloy whose composition is known accurately. This ratio leads to the percentage elemental composition of the sample. To get an accurate compositional analysis, a smooth surface is required. If the surface is not smooth then there is less reflection and the intensity is lowered compromising the technique's accuracy. For a smooth surface the intensity of electrons depends solely on the atomic number.

4.2.1.2 Experimental Procedure for the SEM/EDX Acquisition of Polyphosphates

Small amounts of PAA, SPP and SHMP solid were placed on double-sided carbon sticky tape and adhered to the top of a sample stub. The three samples were then placed into a *Hitachi E1030 Ion Sputter Coater* which evacuated to a pressure of 20 Pa. The chamber was then purged with argon gas and a coating of Pt-Pd (20 nm) was sputtered onto the samples to prevent charging in the electron microscope.

The coated samples were then mounted onto a sample holder and placed on the stage of the specimen chamber of a Hitachi S400 Scanning Microscope, which was evacuated to a pressure of 2×10^{-7} Pa. SEM photomicrographs were taken at the typical accelerating voltage 20 kV at varying magnifications. A photograph of the SEM is shown in Figure 4-2.

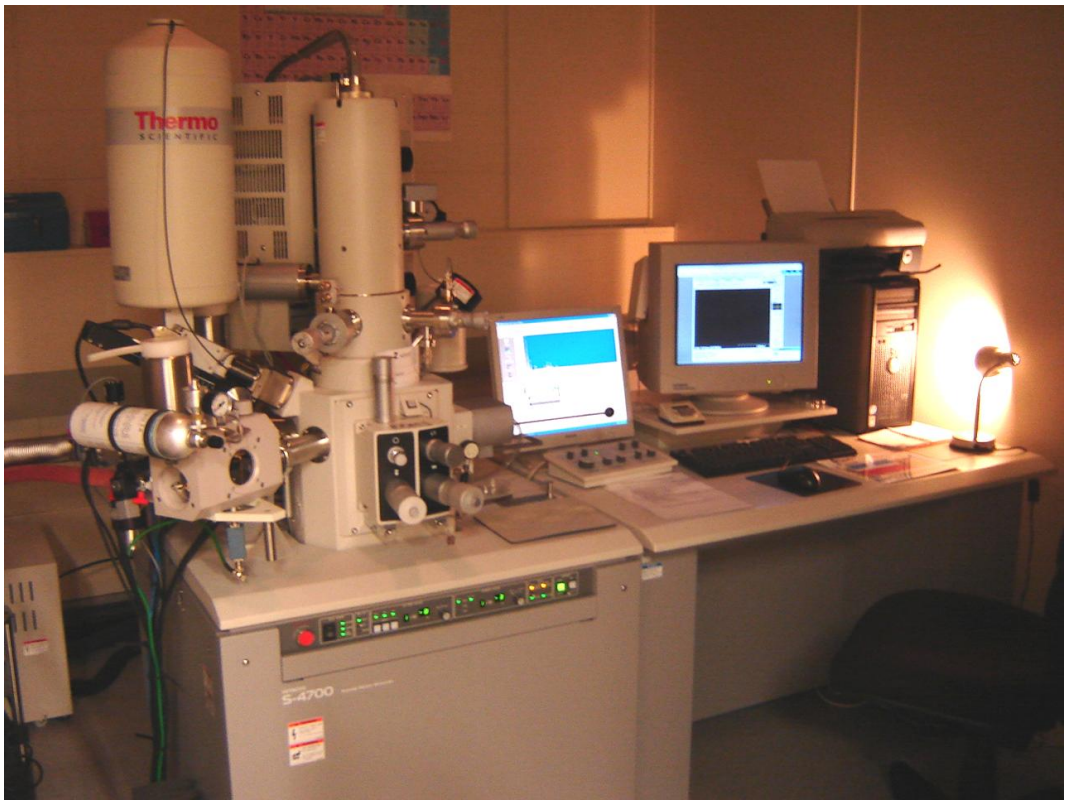


Figure 4-2: Photograph of scanning electron microscope

4.2.1.3 Results and Discussion

SEM/EDX analysis of these samples was anticipated to be difficult because of the challenge in differentiating between SPP and SHMP due to lack of knowledge of the degree of polymerisation and similarities in the chemical formula between the candidates. It was suspected that PAA was made up with a similar formula to SPP but it was not sure whether there were any other additives in the PAA as received that could play a role in its function as a processing aid. The SEM/EDX analysis was conducted to not only try to identify what type of polyphosphate PAA was but also to distinguish if there were any other compounds present.

Figures 4.3-4.5 are EDX spectra of the three polyphosphate samples with a visual photograph of each respective polyphosphate given in Figures 4.6-4.8. Each spectrum show similar portions of phosphorus and oxygen with the phosphorus peak slightly larger on all of them. Also evident in the spectra is a sodium peak. This indicates that the solid must be a sodium salt of a polyphosphate.

Comparisons of the three polyphosphates in terms of EDX-measured peak intensities is illustrated in Figure 4-9. This graph gives an indication that all three compounds are very similar in chemical identity to each other. For PAA and SPP there seems to be a higher proportion of sodium over phosphorus unlike the SHMP sample. In all three samples there was a noticeable amount of carbon present but this can be discounted as it can be traced to the carbon adhesive tape used to mount the samples.

The magnified SEM images in Figures 4.6-4.8 show the solid PAA, SPP and SHMP samples that were analysed respectively. The PAA was sourced from Orica Chemnet Limited in Mt Maunganui. The other two polyphosphates were commercial grade polyphosphates, the SHMP was sourced from the University of Waikato Chemistry Department's internal supply and the SPP supplied by Sigma Aldrich. The SEM images were acquired to see if there were any distinctive differences in the crystal structures between samples. As the image shows, the solid PAA had no distinctive patterns that differentiated it from the other two reference samples apart from the large granules in the SPP sample.

From the information provided from the SEM/EDX studies, PAA was thus proposed to be sodium polyphosphate. This was deduced from the EDX comparison graphs in Figure 4-9. As PAA and SPP have a lower amount of phosphorus compared to sodium, whereas SHMP has slightly more phosphorus than sodium. A further study using infrared spectroscopy, below was used to confirm these results. This also confirms that PAA is incorrectly referred to as SHMP in industry and not SPP.

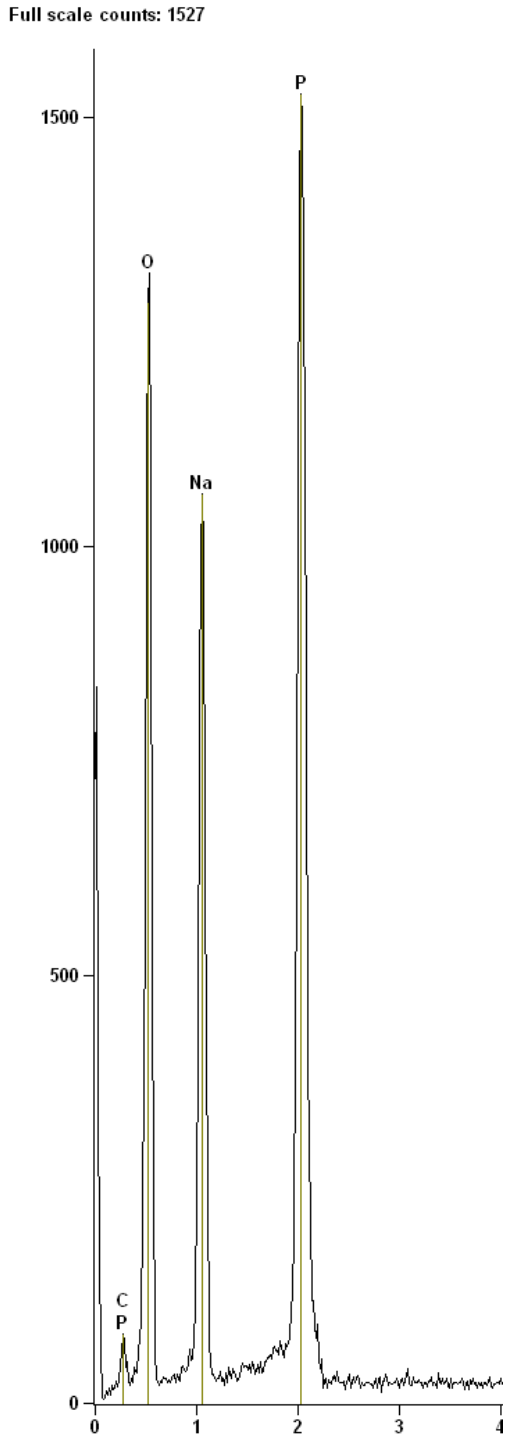


Figure 4-3: EDX spectrum of PAA

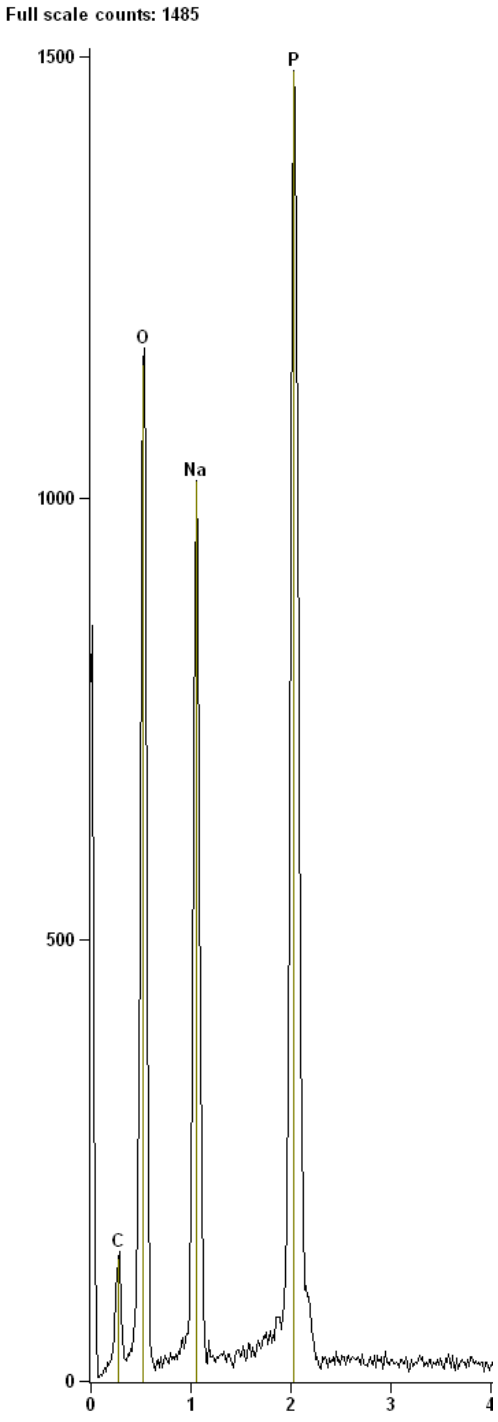


Figure 4-4: EDX spectrum of SPP

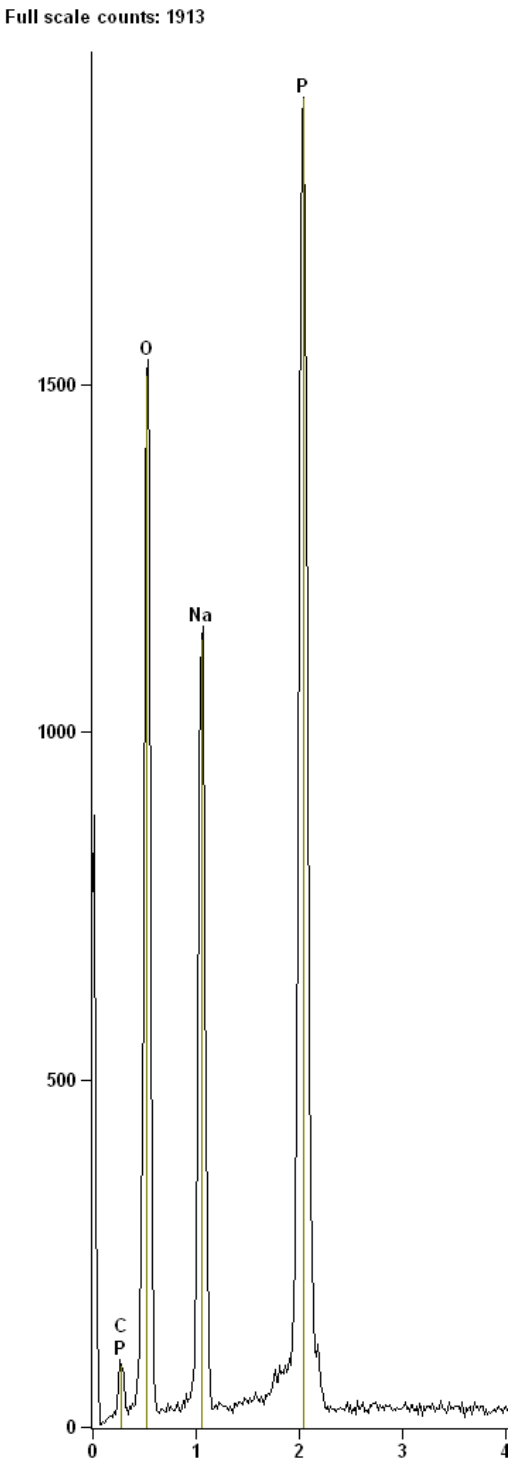


Figure 4-5: EDX spectrum of SHMP

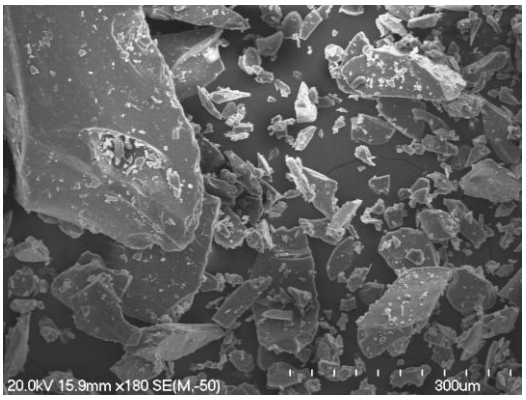


Figure 4-6: SEM of PAA crystals obtained from Hautapu

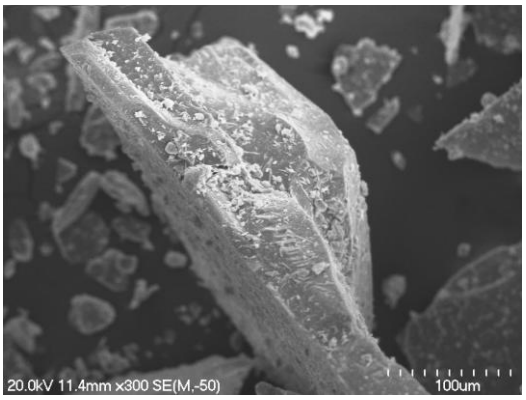


Figure 4-7: SEM of commercially available SPP crystals

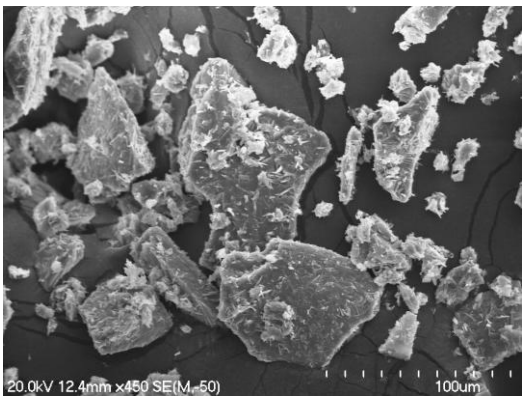


Figure 4-8: SEM of commercially available SHMP crystals

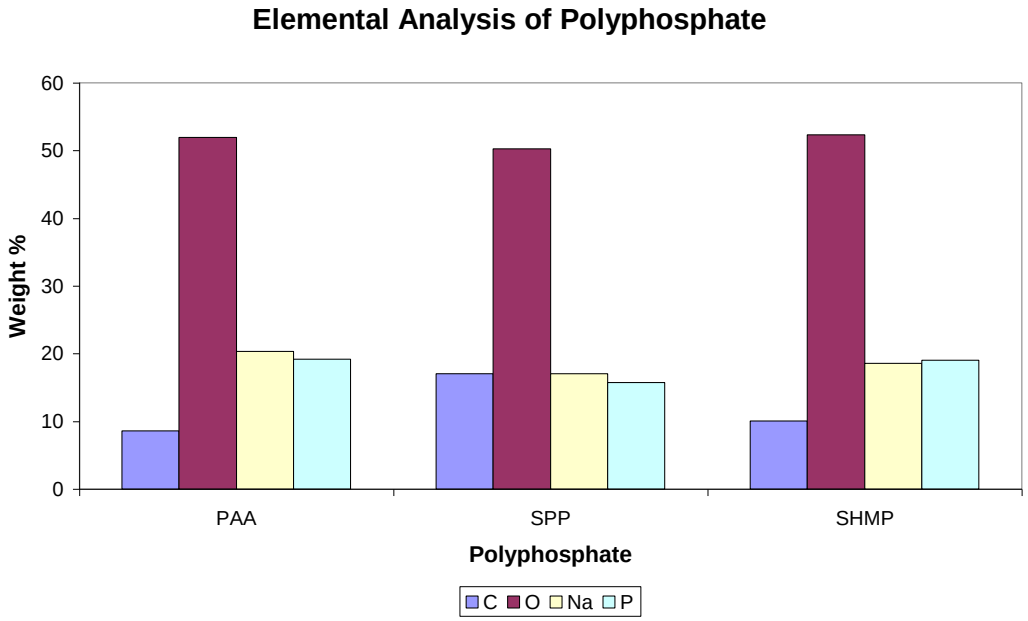


Figure 4-9: EDX elemental percentage comparison of polyphosphates

4.2.2 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transfer Infrared (FTIR) Spectroscopy, also known as Infrared (IR) Spectroscopy is a useful analytical technique that is used in the comparison and identification of chemical substances that contain certain functional groups. This technique was used in this study for two cases. Firstly IR spectroscopy was used as a technique to confirm the conclusions derived from the SEM/EDX analyses on the PAA (and other polyphosphate compounds) and secondly it was used to help identify precipitated solids that formed when solutions of calcium chloride and PAA were mixed.

4.2.2.1 Theory of an FTIR

Infrared (IR) spectroscopy is used for the characterisation of molecules by means of its vibrational spectrum. In molecules, functional groups, such as a carbonyl (CO) group, $-PO_4$, -COOH, $-NH_2$ and many other functional groups can absorb infrared light and appear at characteristic frequencies in the IR spectrum. The spectrum is produced by exposing the sample to IR over a range of wavelengths

measured in wavenumbers (cm^{-1}). Most spectra are acquired over the mid-IR range from 4000 – 400 cm^{-1}. This is a commonly used identification technique since a spectrum for a dry solid sample can take approximately 10 minutes to acquire including sample preparation.

4.2.2.2 Experimental

KBr disks of solid samples were prepared by grinding a small amount of sample with oven-dried KBr with a ratio of approximately 10:1 KBr:sample. Disks were generated by application of pressure (~10 tonne) to the sample mixture. Disks were then analysed by placing into a Spotlight Perkin Elmer 200 FTIR spectrometer system and scanning from 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. Several solid sample analyses were undertaken for this study.

IR Analysis of the Source Polyphosphate Salts: The three polyphosphates; PAA, SPP and SHMP were each prepared separately by grinding a small amount with KBr, as described above, in a mortar and pestle and pressing into a disk. An absorbance spectrum was run which acquired scans over a one minute duration.

IR analysis of the Calcium Salts of the Polyphosphates: In a simple test tube experiment ~0.5 g of SPP was added to 20 mL of distilled water with ~1.5 g of dissolved $CaCl_2$ to ensure that a precipitation formed. The resulting precipitate was filtered and dried in a 60°C oven overnight. The same experiment was carried out with PAA that was supplied from Orica Chemnet Limited. The resulting solids were pressed into a KBr disk and analysed By FTIR.

4.2.2.3 Results and Discussion

For the identification of PAA, three IR spectra were run to help reinforce the conclusion made from the SEM/EDX analysis. The IR spectrum, given in Figure 4-10, showed conclusive evidence that PAA was in fact SPP. The two spectra showed every peak to be virtually identical with characteristic peaks and shoulders. This was in disagreement from what the industry knows PAA as, giving it the industrial name of SHMP. This was also supported by a review by Rashchi and Finch mentioned earlier in this Chapter 2.

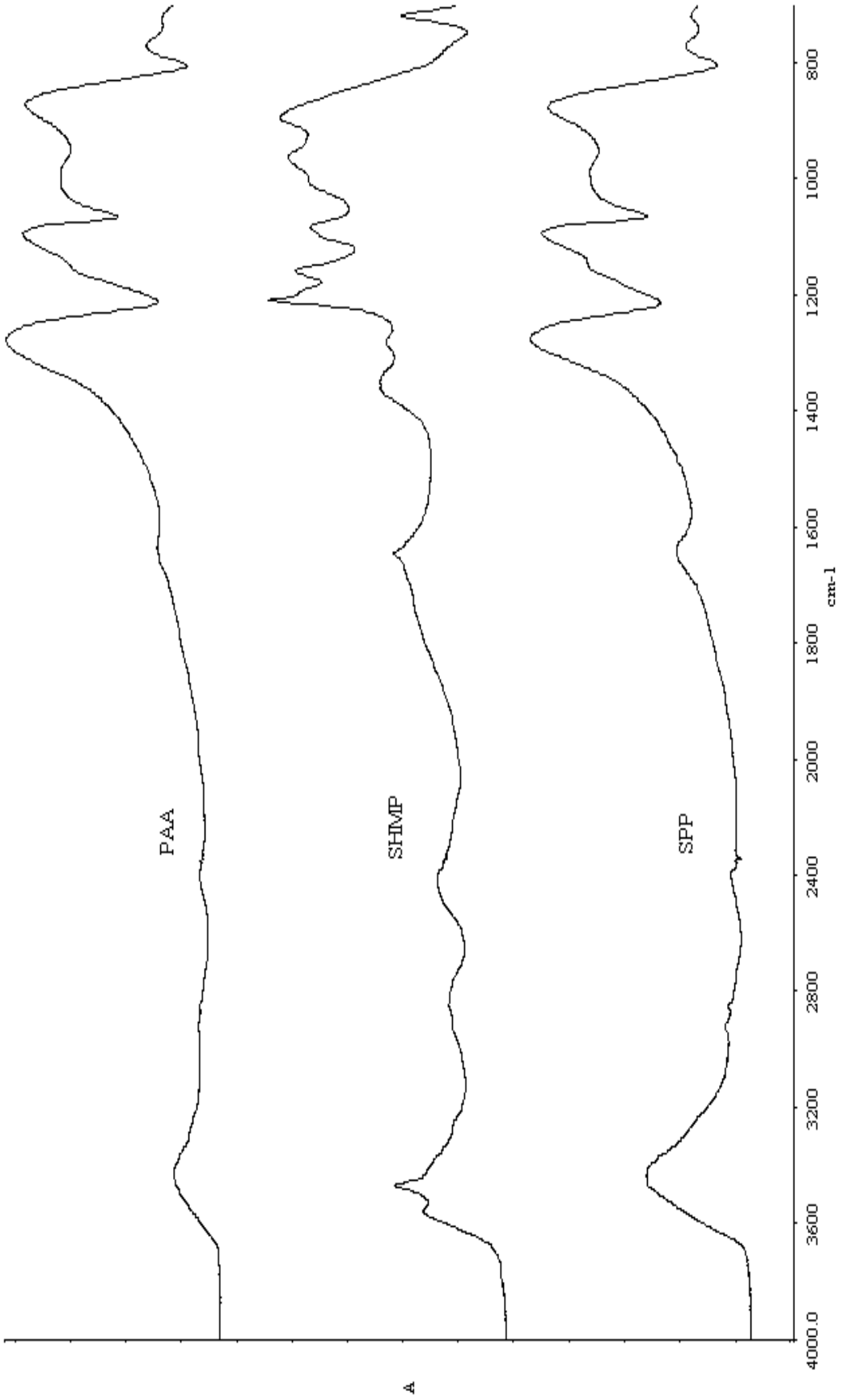


Figure 4-10: IR spectra of polyphosphates a) PAA, b) SHMP and c) SPP

Once PAA was chemically identified it was important to confirm the findings of the calcium polyphosphate salt that was observed when PAA was added to a solution of calcium chloride. This was done by isolating the Ca-PAA salt and also making and isolating a Ca-SPP salt. This provided further validation to the identification of PAA as being SPP.

The spectra shown in Figure 4-11, shows the comparison of Ca-SPP precipitate with Ca-PAA precipitate. Both have very similar features with major distinctive peaks at ~1266 cm^{-1}, ~900 cm^{-1} and ~535 cm^{-1} as well as other minor peaks. This is in direct contrast to the IR spectrum of sodium hexametaphosphate which showed distinctively different features. The two spectra give comparative evidence of the identity of the polyphosphate precipitation with calcium and also give validation to the initial SEM/EDX experiment confirming that PAA had the same chemical composition as SPP.

The importance of identifying PAA as being purely Sodium Polyphosphate eliminates the possibility of any other compounds that may have been present in the processing aid. Positive characterisation also allowed more relevant information of PAA to be established and further literature to be sourced, which was discussed chapter 2.

It was also important to make relevance to whey permeate. It was observed that when PAA was added to filtered whey permeate at the standard dosing rate of 0.4% w/w, there was a persistent, instantly formed precipitate. To confirm that this solid was the Ca-PAA salt it was isolated by filtration and dried in an oven. A Ca-PAA solid made from adding 1 g of PAA to 100 mL of water containing 5 g of calcium chloride was also filtered and oven dried. An IR spectra were taken of the two and the results are given in Figure 4-12.

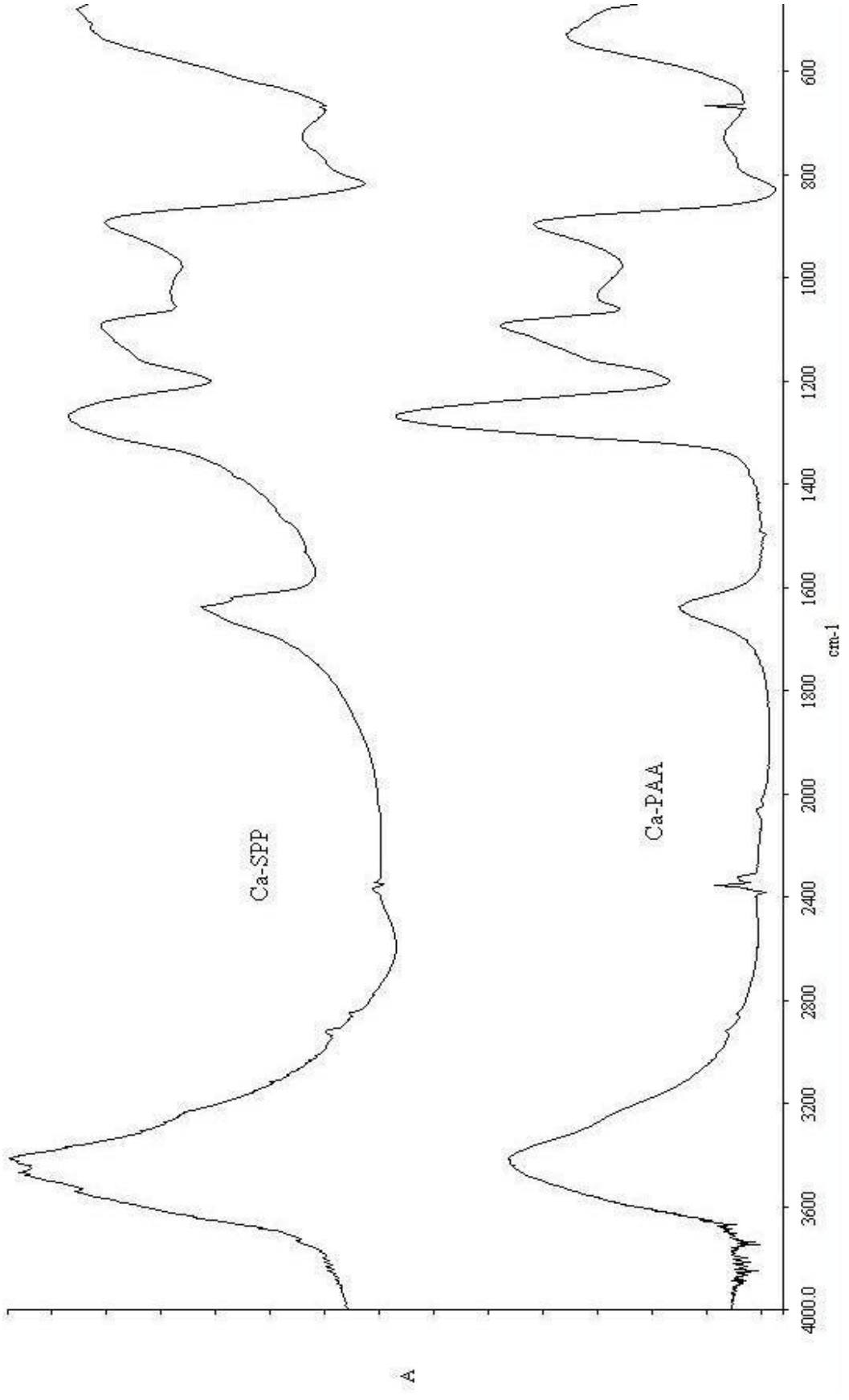


Figure 4-11: Infrared spectra of calcium polyphosphate salts: Ca-SPP salt (a) and Ca-PAA salt (b)

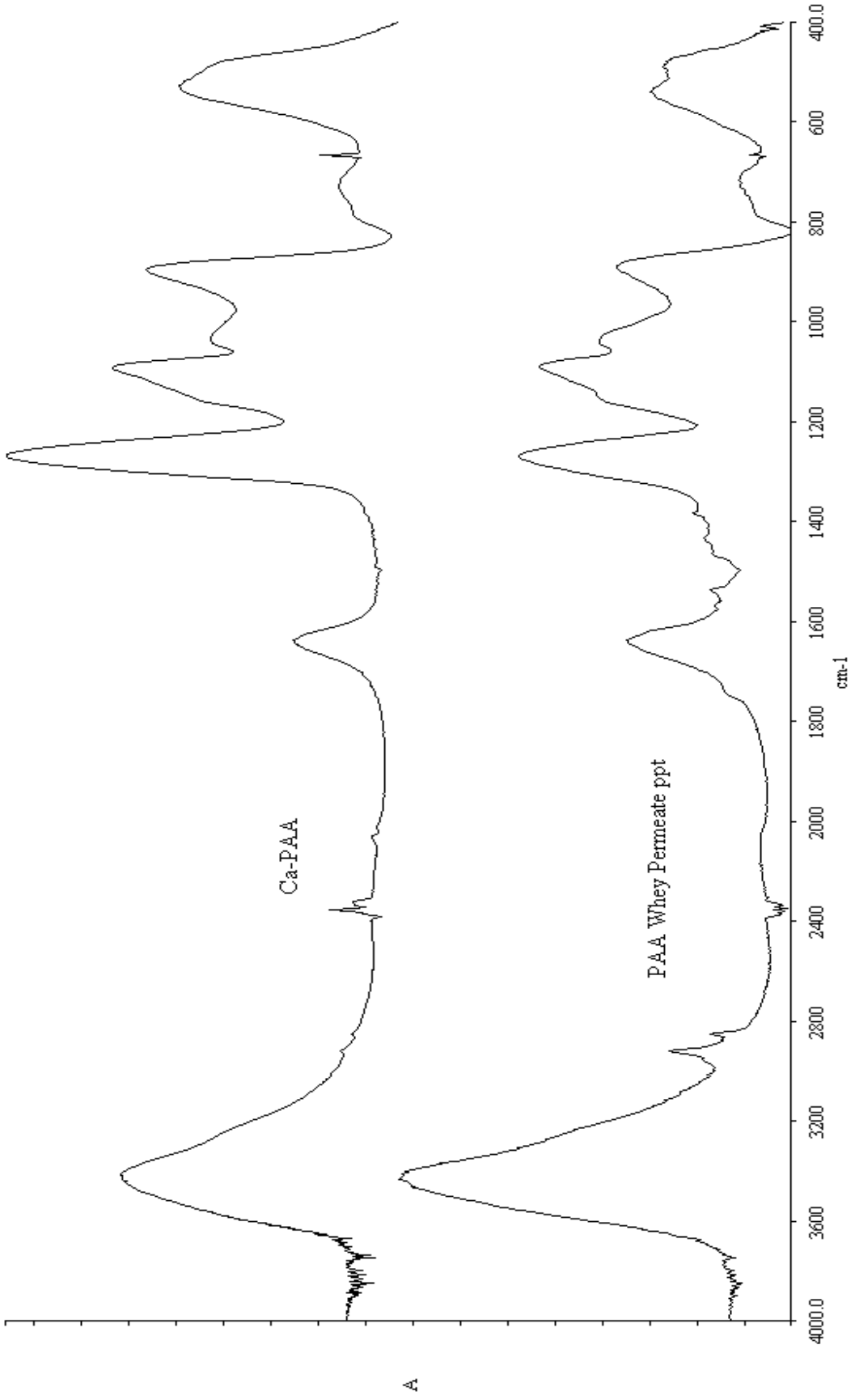


Figure 4-12: Comparison of IR spectra a) PAA-calcium solution precipitate

b) PAA-whey permeate precipitate

The two spectra were compatible giving further evidence that PAA forms a calcium salt when added to whey permeate. In the whey permeate spectrum there are signs of other peaks that are due to other compounds in the whey permeate. The C – H stretches in the area of 2800 – 3000 cm^{-1} correspond to the same stretching frequencies that is seem in lactose (Figure 3-5). Lactose would be the most obvious interference from a whey permeate sample. The evidence that was shown in this section relating to IR spectra and SEM/EDX data were used to establish as clearer understanding and identification of the role of PAA with whey permeate.

4.2.3 pH Stat and Turbidity

The precipitation of PAA with calcium ion was studied more quantitatively by using a pH-stat approach. The pH-stat was used to eliminate the variations in pH that were observed to occur in the reaction solution after precipitation had commenced (the preliminary results of which are given in this section). Furthermore, to study the formation of the calcium PAA salt in greater detail the monitoring of turbidity was also used in some experiments to help track the formation and persistence in solution of any precipitate formed.

4.2.3.1 Theory of pH Stat and Turbidity

pH-Stat System: A pH-stat is used to help control the pH as a variable for experiments. In modern instrumentation, it is usually a computer controlled system that adjusts the amount of base introduced into the sample system to control the pH. The base, which is usually 0.01-1 mol L^{-1} NaOH, is introduced via a 10 mL automated burette (see Figure 4-13). The desired pH is entered into the computerised controller unit and the pH-stat system then functions to keep the pH constant by automatically adding the sodium hydroxide when the pH starts to drop below the stipulated value.

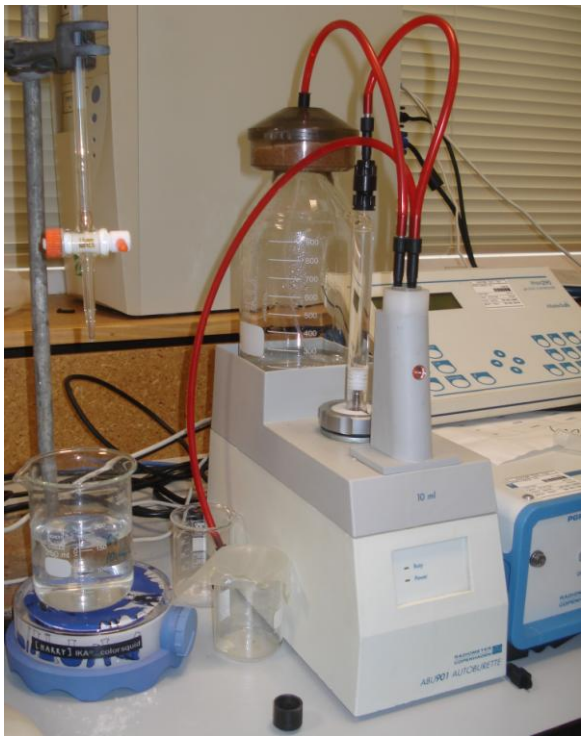


Figure 4-13: Photograph of pH stat system

Turbidity UV/VIS: Turbidity can be used as a qualitative measure of the amount of precipitation in solution. Instruments dedicated to the measurement of suspended particles in solution are normally called "Nephelometers" but in the absence of these, turbidity can be measured customarily with a standard double beam UV-Vis. Spectrophotometer. A light of specific wavelength is passed through the sample placed within a sample cuvette of 1cm path length. The reference blank is a cuvette of distilled water. Any sample that has a precipitation suspended in solution will scatter some of the light reaching the detector to a degree dependent on its particle size which will register in the detector as "absorption" of light. The magnitude of the absorbance at the arbitrary wavelength chosen is proportional to the amount of precipitate that is suspended in solution.

4.2.3.2 pH Stat Studies: Experimental Procedures

pH-Stat System: The pH was measured using a Radiometer glass electrode in combination with a Radiometer "red rod" (AgCl/Ag) reference electrode connected to Radiometer PHM290 pH stat controller. The pH was initially

adjusted to a value below 4.7 (the pH that acid whey permeate exists at in the dairy factory streams) with dilute HCl and kept at pH 4.7 ± 0.2 throughout the titration. 0.01 mol L^{-1} NaOH was injected via a 10 mL automated burette controlled by ABU901 Autoburette Radiometer pH-stat system. *Microsoft Windows 95* was used to control the pH stat system at all times.

Turbidity Measurements on the UV/VIS Spectrophotometer: For turbidity measurements, a 1 cm wide plastic cuvette was used to hold the sample. A single wavelength absorbance reading was recorded at 420 nm on a double beam Cary 1 UV-Vis Spectrophotometer. Distilled water was used as a reference blank. Samples were usually taken from the experimental flask and run within 1 min of collection. The solution in the sample cell was swirled prior to placing into the spectrophotometer to minimise any sedimentation or settling which would have led to lower values of turbidity.

4.2.3.3 Preliminary pH Experiment

The rationale for controlling the pH during precipitation reactions of Ca ion with PAA solutions came about when a titration involving a calcium solution was added to a solution of sodium polyphosphate. There was a noticeable decrease in pH with time after addition of the PAA which had to be compensated for in future experiments.

Experimental: 1 g of SPP was dissolved in 100 mL distilled water. A 0.1 mol L^{-1} solution of $CaCl_2$ was added via a 50 mL burette and the pH was monitored without pH-statting. The titration was carried out in triplicate.

Results: Figure 4-14 shows the decrease in pH when calcium is added to a SPP solution. The initial pH was adjusted to ~4.5, which is the value of acid whey permeate. The graph shows an initial linear drop before gradually levelling off to an approximate pH value just above 3.

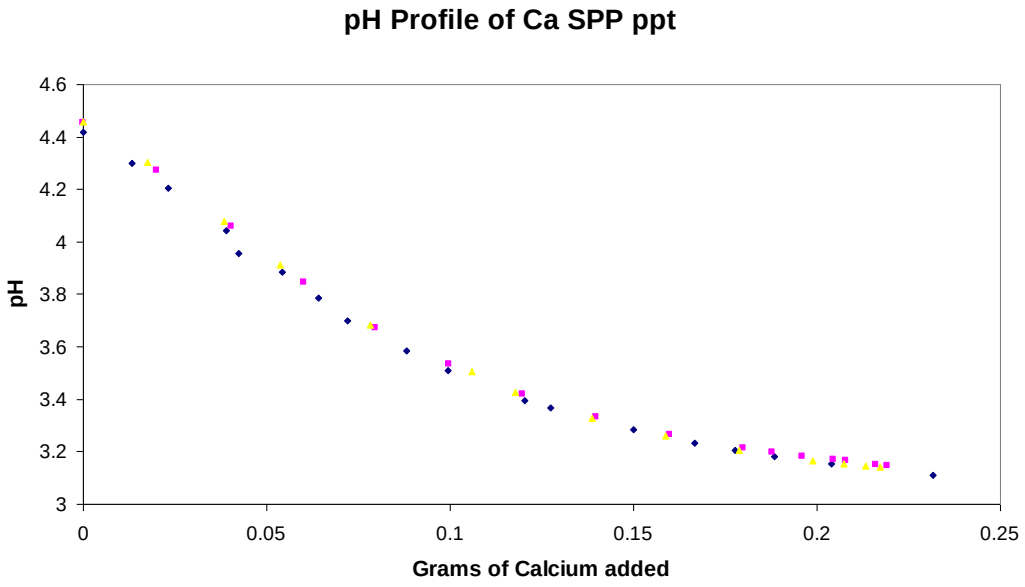


Figure 4-14: Reduction of pH when calcium solution is added a SPP solution

It should be noted that after the experiment had finished, an attempt was made to increase the pH back to its original value from 3 back up to 4.7. When this was done using NaOH the amount of precipitate increased considerably to the point where it formed coagulated lumps. This is investigated further in this chapter (Figure 4-18). It was not sure as why the pH decreased but it could be a result of H^+ ions being liberated from the SPP as it sequestered calcium ions from solution. This would suggest that SPP would not be a pure sodium salt as some of the oxygen groups could be occupied by hydrogen ions. Calcium could possibly be exchanging with the hydrogen ions by having a higher affinity for the SPP anion.

4.2.3.4 Effect of PAA Concentration

To get a better quantification of PAA and its calcium tolerance, an experiment was set up to show the relationship between the concentration of PAA and its ability to stay soluble in water containing high concentrations of dissolved calcium ion. This experiment was set out to determine the point of precipitation after the addition of a calcium solution to known concentrations of PAA solutions. There is a distinctive point at which a persistent white precipitate is observed to form in solution, which compromises the efficiency of PAA in solution, to act

ostensibly as a soluble calcium ion complexing agent, by removing it from solution as an insoluble salt.

Experimental: The experiment was carried out on four known concentrations of PAA, that were made up in the laboratory from the solid sample received from Orica Chemnet, with the addition of a 1 mol L^{-1} calcium nitrate solution. A 1 mol L^{-1} solution of $Ca(NO_3)_2$ (APX Ajax Finechem analytical grade) solution was titrated into a series of four PAA solutions. Each PAA solution contained 0.25 g, 0.5 g, 0.75 g and 1 g of PAA respectively dissolved in 50 mL of type 1 (Millipore) distilled water, in a 150 mL beaker. The experiment was carried out at room temperature and the end point was determined visually by the detection of a persistent, distinct white precipitate. Additionally, pH was held at pH 4.7 via control by a pH-stat system.

Results: When precipitation occurs with PAA and Calcium ions, it was observed from the earlier non-pH-statted beaker experiment that there was a noticeable decrease in pH, see Figure 4-14. This was made evident by the response of the pH-stat system during the pH-controlled precipitation as the pH stat tried to maintain a pH of 4.7 in the solution by adding more NaOH.

When a pH stat experiment is performed the amount of NaOH that is added to the system is controlled by a computer program. This introduces the base to the system when the pH is detected to drop below the set level of 4.7. An example of a screenshot, which gives the details of the experiment and the recorded pH along with the amount of NaOH added to maintain the pH, is given in Figure 4-15.

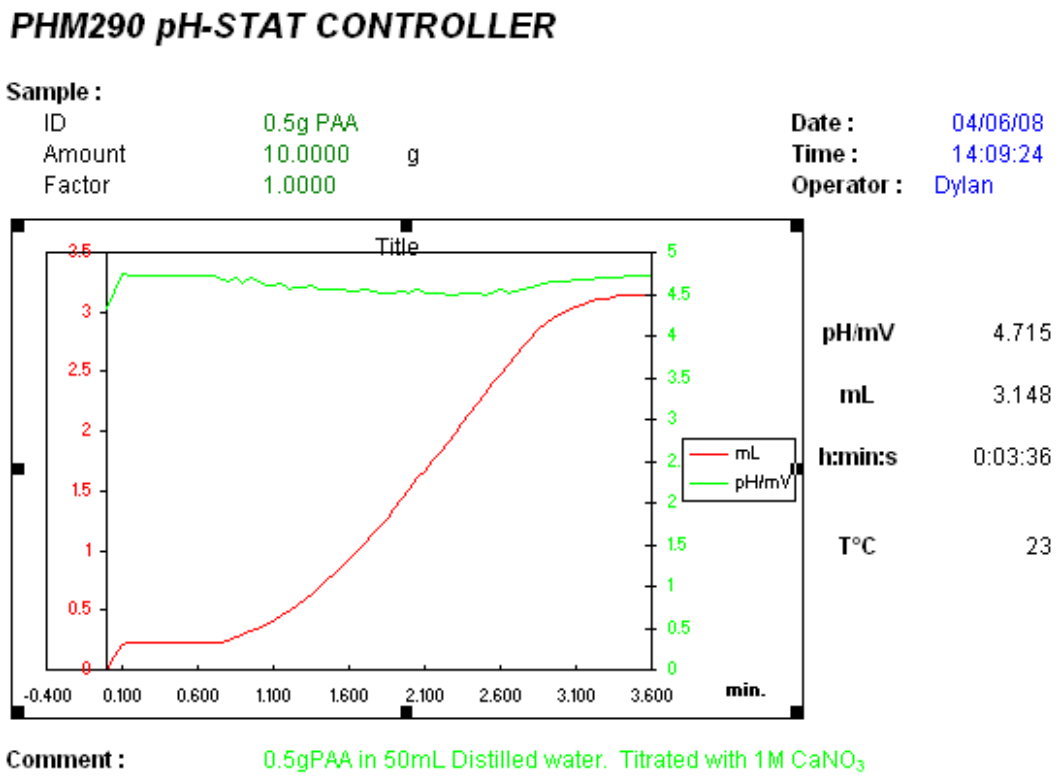


Figure 4-15: Example of a screenshot from a pH stat printout

On an industrial scale, since there is a large volume of whey permeate, compared to the amount of precipitation due to PAA in the evaporator, there would be a much less noticeable change in pH. This lack of pH change would also be due to the higher buffering capacity of whey permeate due to the presence of citrates and other species which can counteract any overall pH changes via their own acid ↔ base equilibrium.

When the calcium was titrated into the PAA solutions there was a tendency for the pH to decrease. This pH drop is suppressed with the pH stat system by introducing the NaOH to maintain the pH at 4.7. Figure 4-16 shows the amount of NaOH that was needed to maintain a constant pH and also the point of precipitation from the added calcium solution for each of the four PAA concentrations trialled with the pH-stat-controlled precipitation.

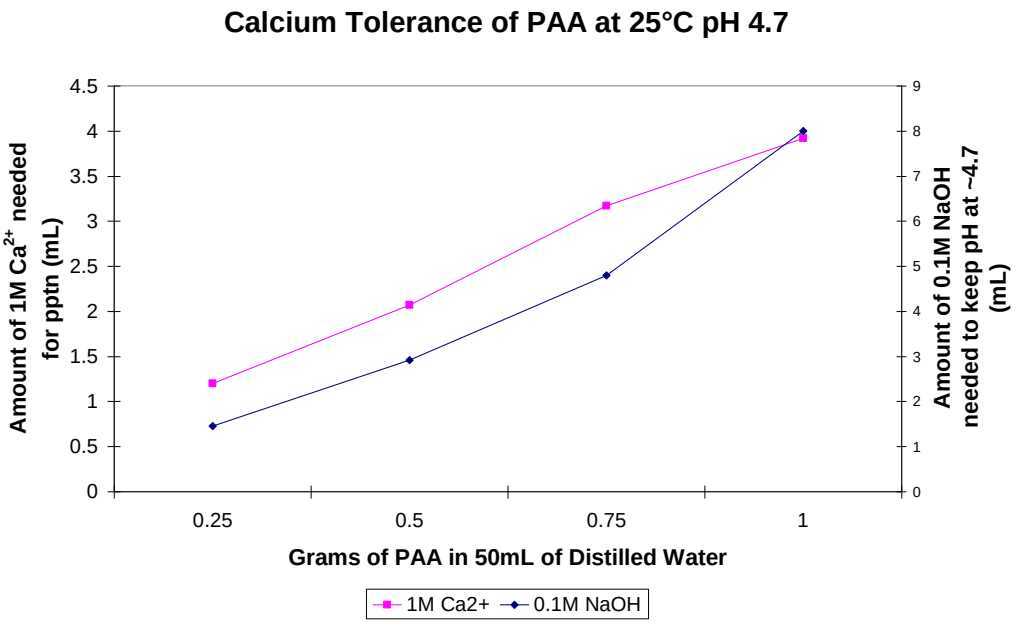


Figure 4-16: Amount of 0.1 mol L^{-1} NaOH used in PAA calcium titration

The addition of NaOH was important in finding a trend that related to the amount of calcium required to form a persistent precipitate with PAA that was independent of pH. Figure 4-17 shows the result of adding calcium to known amounts of PAA, there is a linear correlation between the amount of free calcium ions required to form a persistent precipitate and the concentration of PAA.

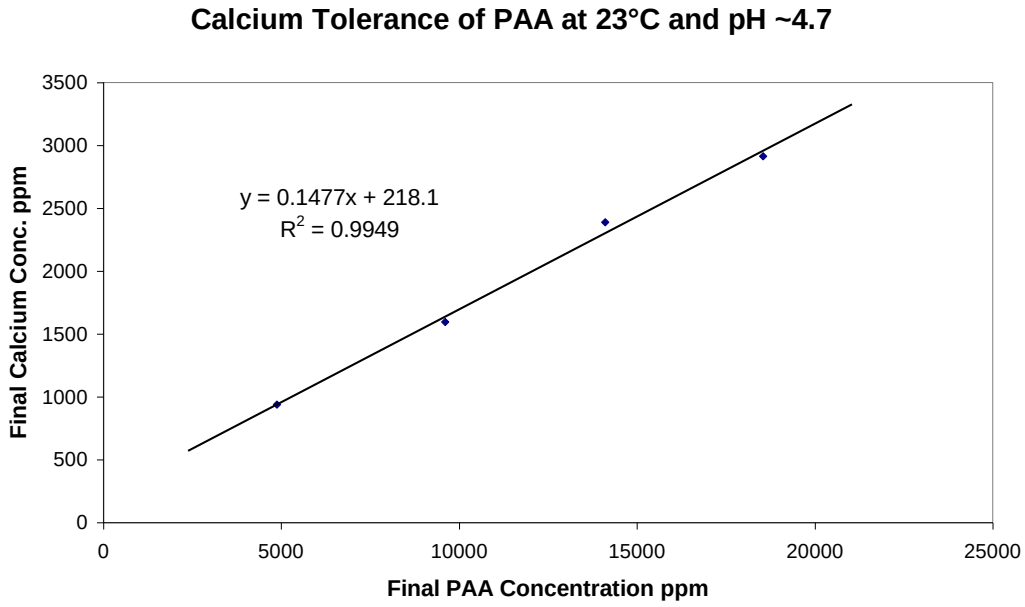


Figure 4-17: Calcium tolerance point of PAA

The above graph can be used to help give an assumption with whey permeate. When PAA is added to whey permeate there is evidence of the same Ca-PAA precipitate. The lactose processing plant at Hautapu doses PAA at rate of 0.4% on a weight basis. This means that for every 1kg of total solids that enters the evaporator 4g of PAA is added. The 4g of PAA is added to the product as a solution and becomes diluted by the whey permeate feed stream. Table 3-2 gave a clearer description of the PAA and feed stream concentration. The table also compares other dosing rates with 0.8% being used at other lactose production plants within Fonterra.

The line equation in Figure 4-17, can be used to give a qualitative indication of how much calcium is bound by PAA as it has precipitated out of the whey permeate. The equation can be extrapolated to the levels of PAA in the evaporator. The assumption that is made is that the linearity of the precipitation point carries through down to these levels. When taking into consideration the linearity of PAA vs. calcium tolerance and assuming that the linearity still holds at lower values of PAA concentrations, a theoretical free calcium limit at 23°C can determined.

The equation $y = 0.1477x + 218.1$ is taken from the linear plot of calcium tolerance above, where x is the final concentration of PAA in solution. This can be transcribed to a whey permeate feed stream where PAA has a concentration of 840 ppm (with a dosage rate of 0.4%). Using this value to find the maximum of calcium ion that can be added with forming a precipitate (y) gives a free calcium concentration limit of 342 ppm. This value gives a very approximate indication of the amount of free calcium that needs to be present to bind up PAA. As free calcium levels in whey permeate are reported to be up around 900ppm (Chui, 2007), it is evident that the ability of PAA to act as a soluble calcium ion sequestrant, like EDTA is for instance and as envisaged by Fonterra, must be placed into doubt. Now it is important to note that the “900 ppm” of total calcium expected to be present in a typical whey permeate stream is not all in a free ionic form as it is in equilibria as a bound ion in a number of other species, this can come about from citrate normally present in the whey permeate and the calcium

can also be bound up with other mineral ions like sulphate and orthophosphate. This complication was seen earlier with respect to accurate calcium ion measurements using the ion specific electrode. Without literature on the solubility product of calcium polyphosphate and pK_a values of polyphosphoric acids, it is difficult to present thermodynamically based arguments on the driving force for the precipitation of the Ca-PAA salt from solution.

4.2.4 Effects of pH on the Precipitation of Calcium Polyphosphate

From previous experiments it was clear that pH has an effect on the precipitation of calcium polyphosphate salts. Upon addition of calcium to a PAA solution it was noted that the pH decreases. This is due to the possibility that the protons on the polyphosphate ion in solution are being displaced by the free calcium ions that coordinate to the polyphosphate to form the precipitate. In early tests probing the precipitation of PAA out of solution as a calcium salt, it was noted that once a precipitation had formed and the pH raised back to its original value, by addition of dilute NaOH, more precipitate was observed to form until it transformed from merely a turbid solution to a more murky solution with visible coagulated lumps. The experiment outlined below was designed to determine whether testing a range of fixed (via pH-stat control) pH values of the precipitating Ca-PAA solution system would have any effect on the persistent precipitation endpoint.

Experimental: The experiment was carried out on a series of PAA solutions where 0.5 g of PAA was dissolved in 50 mL of "type 1" (Millipore) water. 1 mol L^{-1} $CaCl_2$ solution was used as the titrant. The pH was adjusted to a value that was kept fixed via pH stat control in the pH range 4 – 9.

Results: The precipitation reaction studied at variable fixed pH gave some unexpected results in both acidic and basic environments. It was postulated that the calcium tolerance point of the titration would decrease as the pH increased, since at a higher pH less calcium would be needed to precipitate out the polyphosphate, because of the increase in precipitation when the pH was raised at the endpoint of the previous experiments (Figure 4-14). Instead there seemed to

be two distinct patterns that emerged, which are shown in Figure 4-18. The graph shows the level of calcium ion that was needed to form a persistent precipitate at specified pH values.

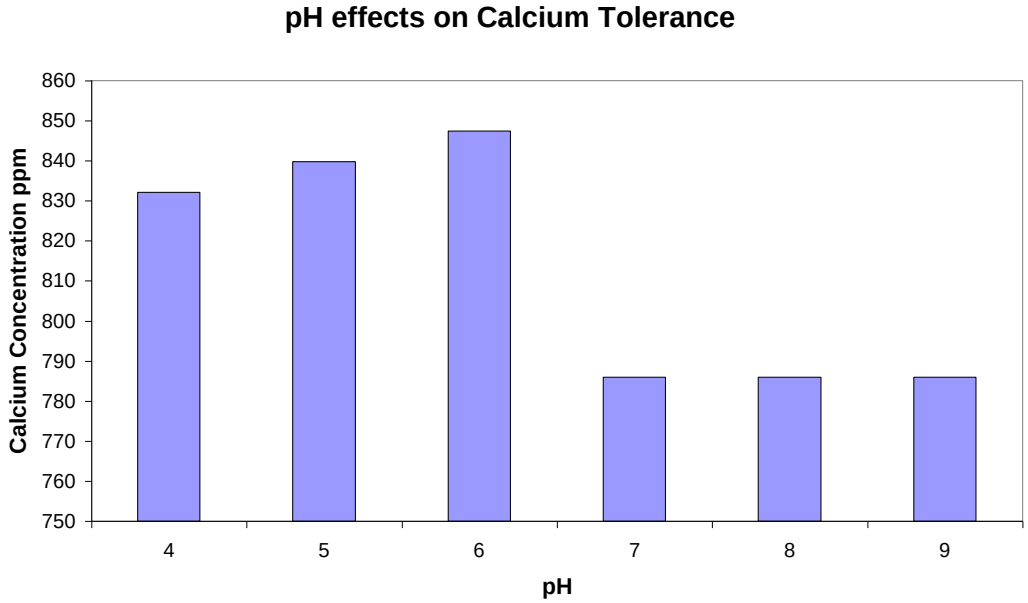


Figure 4-18: Calcium tolerance of PAA at specified pH values

It was obvious that calcium tolerance at the higher more alkaline pH values was lower than at the lower pH values as expected. However, at pH below 7, the calcium tolerance point actually decreases slightly in the range from pH 6 to pH 4, this means that polyphosphate (in acidic solutions) is more likely to stay in solution when the acidity is weaker. Hence at pH 4 the calcium tolerance point was 832 ppm of calcium, however this tolerance level increased up to 847 ppm at pH 6.

When the calcium tolerance was tested in basic pH range from 7 – 9, there was a dramatic change in pattern of the tolerance point. The point of precipitation dropped to a constant level of approximately 786ppm. This suggests the amount of OH^- ions may have an important role in the formation of the calcium polyphosphate salt.

A possible deduction that can be drawn from these results is the possibility of two competing reactions. In basic conditions there is very small levels of H^+ ions in solution that are able to bind to the PAA. This leaves sites free on the PAA for calcium ions to bind to and hence precipitate out of solution. In acidic conditions there could be competition between the H^+ ions and Ca^{2+} ions binding to the PAA. When H^+ is occupying a charged O^- site on the polyphosphate then the PAA is soluble. When a precipitate is present there is a noticed continual reduction in pH. This could be because the Ca^{2+} ions that are still in solution are liberating more H^+ into solution as more PAA is slowly precipitated out.

The proposed theory above however does not account for the fact that there is an increase in tolerance when the acidity is lowered from a pH value of 4 up to 6. An IR analysis of the precipitates shown in Figure 4-19 show the precipitate formed over the ranges of pH to be identical. Further investigation is needed in the future to justify the proposed theory but with a lack of solubility product data such as the ion product and KSp values it is difficult to make form some thermodynamically based arguments to explain this behaviour.

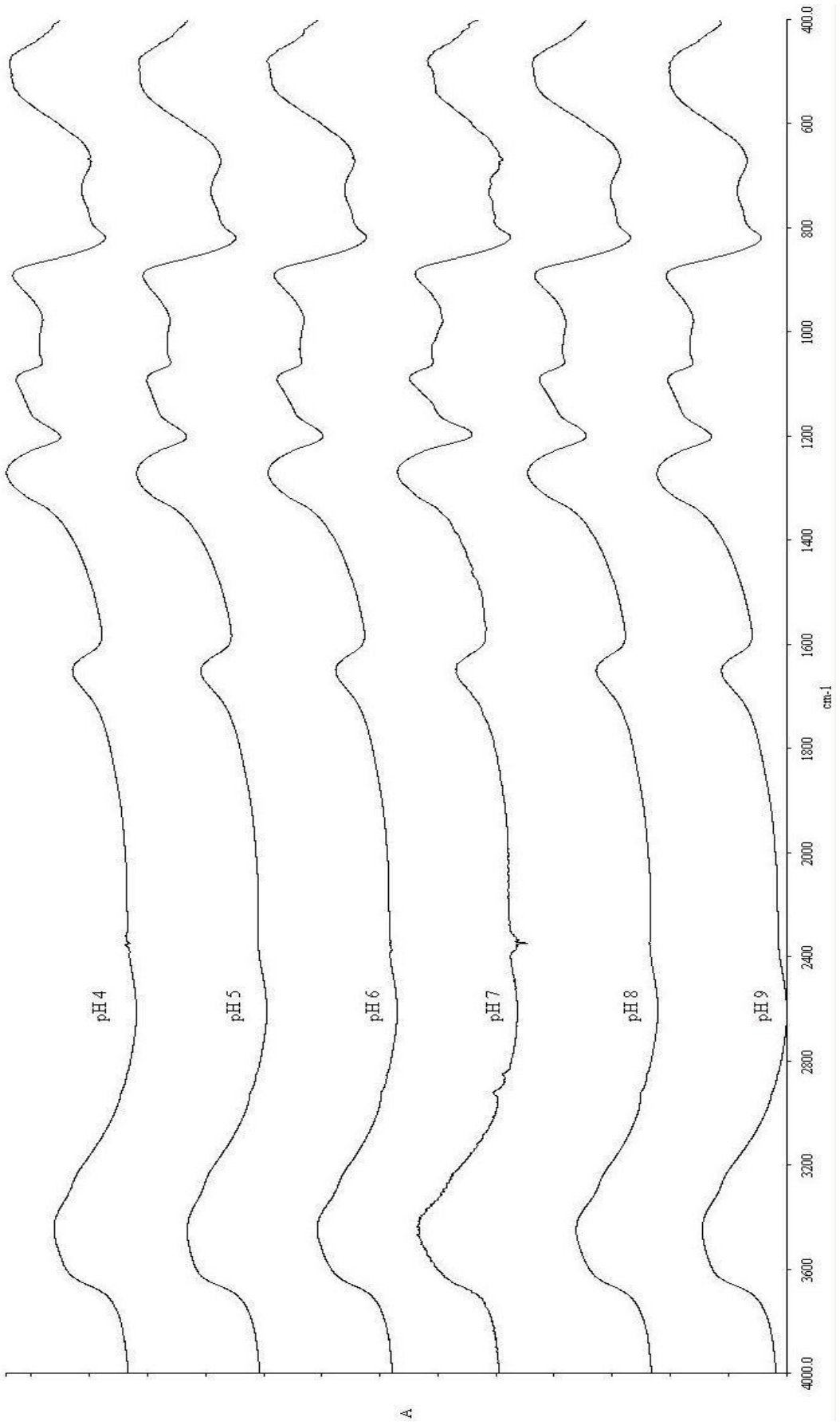


Figure 4-19: IR spectra of Ca-PAA precipitate formed over a pH range of 4-9

4.2.5 Transmittance Readings of Ca-PAA Precipitate

4.2.5.1 Replication of Amjad *et al.'s* Calcium Tolerance Experiment

Calcium tolerance has also been demonstrated by Amjad et al. on a number of other scale inhibitors used in the water industry. This section attempts to replicate his experiment and to see if the same experiment can be applied to PAA. As a way to quantify the amount of precipitate a method was followed that looked at the increase in turbidity with the amount of polyphosphate added to a calcium solution. This was modelled on a method carried out by Amjad *et al.* (Amjad et al., 2003), that focussed on phosphonates. Amjad *et al.* discussed that polyphosphates are used in water treatment processes to inhibit the formation of scale forming salts. The authors of that paper also mention the superior stability of phosphonates vs polyphosphates under the extremes of pH and temperature but acknowledge that both have poor calcium tolerance.

Experimental: A series of 250 mL beakers containing 100 mL of 250 g/L calcium solution was dosed with varying amounts of PAA concentration from 0 to 400 ppm. The temperature was kept at a room temperature of 21°C. The pH was adjusted to 9.5 but it was difficult for the pH to stabilise because of the pH lowering which was seen in previous experiments. After the PAA was added, a wait of 30 minutes was needed to help reach equilibrium, after which a homogenous transmittance reading was taken at 420 nm using a UV/Vis spectrometer.

Results: As a reference point for PAA the concentrations of 1-Hydroxyethylidene-1,1- Diphosphonic Acid (HEDP), that was used in Amjad's experiment was applied to the initial experiment which meant that a concentration range of 0 – 40 ppm was used. The results of Amjad *et al.* Ca-HEDP experiment along with the results obtained with PAA are compared in Figure 4-20. The low concentration of PAA (up to 40 ppm) did not give any visible precipitate. Because of this the concentrations of PAA were extended out to 400 ppm (as defined in the experimental). This finally gave a noticeable reduction in turbidity. For these readings the point at which the experiment was halted was when the transmittance

reading reached a plateau at 40 %. This plateau was thought to be the end of the experiment but it was later found that the precipitate would redissolve if more inhibitor was added reducing the turbidity. In this case the plateau turned out to be a minimum that will be explained later in the section.

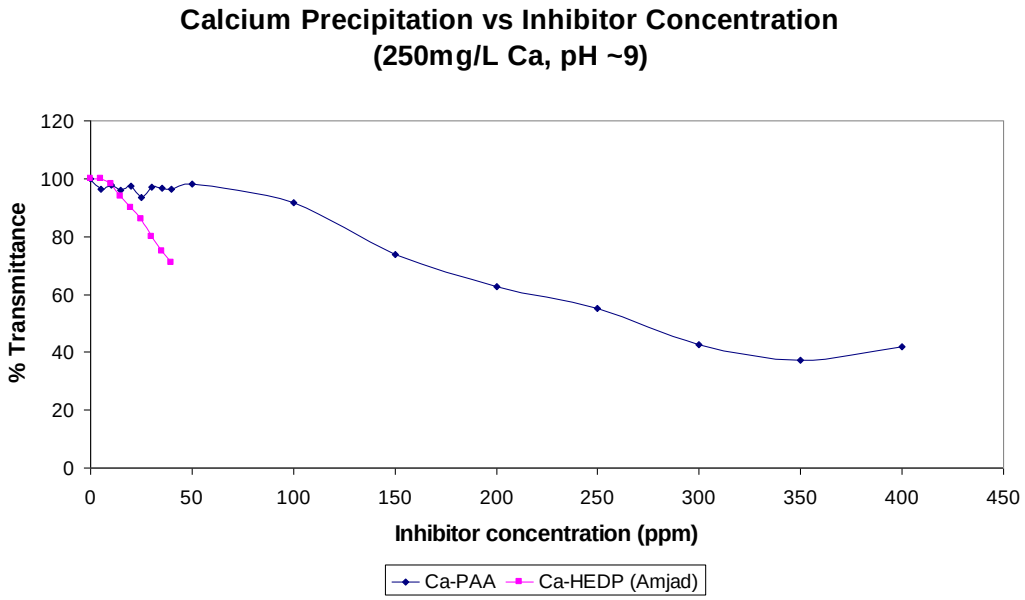


Figure 4-20: PAA precipitation with comparison to Amjad *et al.* Ca-HEDP salt

4.2.5.2 Re-Dissolution of Calcium Polyphosphate

This section looks at the extension of Amjad's experiment as it was noticed that when calcium ions were in excess of PAA in solution there was a noticeable amount of precipitate. However when more PAA was added, the precipitate redissolved. An experiment was designed to look at how much PAA was needed to dissolve a known amount of calcium ions.

Experimental: This experiment is a replication of the one previous, based on Amjad *et al.* calcium tolerance. The difference is that the pH was altered from ~9 in the previous experiment to 4.7 in this experiment. This was to replicate the pH of acid whey permeate. This experiment was also extended to include the dissolution of the Ca-PAA precipitate.

Results: The results shown in Figure 4-21 illustrate the re-dissolution of the Ca-PAA precipitate when the concentration of PAA increasing from 400 ppm up to 1000 pm. The results show a similar pattern in the first half of the curve to what Amjad *et. al.* presented. The experiment also illustrates the redissolving of the precipitate when more PAA is added. This phenomena is also mentioned earlier in this chapter when Burgess (2004) witnessed that the precipitate was not present at high concentrations of PAA.

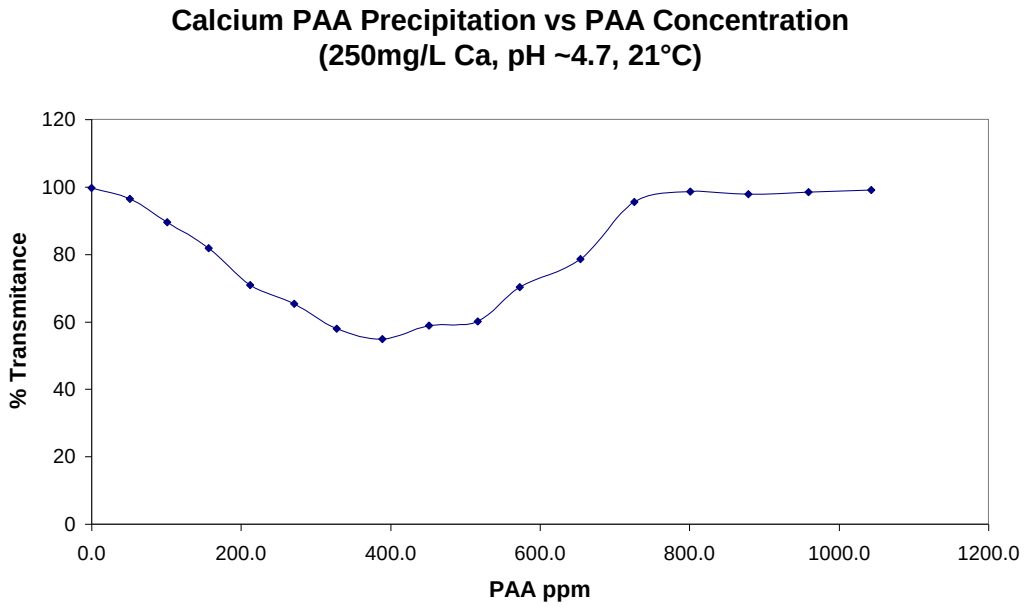


Figure 4-21: Transmittance reading of PAA precipitation

A possible explanation of the results in Figure 4-21 is that a precipitation is only formed when the PAA is saturated with calcium ions. When all available sites are occupied by calcium ions, that is one divalent calcium ion per two phosphate monomer units in the chain, then a solid will form. This theory can explain both trends in the graph with the first being the decrease in transmittance and the second, where the precipitate re-dissolves.

When a small amount of PAA is added to the calcium solution all of the PAA precipitates. The transmittance readings are initially high because there is not enough PAA added to scatter the light sufficiently. As more and more PAA is added then the precipitate becomes more noticeable. This eventually reaches a

maximum, where all of the calcium ions in solution saturate all of the PAA resulting in the lowest transmittance reading of ~50% transmittance.

After this point, any more PAA that is added to the solution can help reduce the saturation of calcium ions on PAA. In other words, when the calcium ions neutralise the negative charges on PAA it becomes insoluble but when there are more PAA molecules the calcium ions can redistribute over all of the available PAA to give an overall negative charge, which causes it to become soluble again.

This theory gives an explanation of how PAA interacts with whey permeate. Because the calcium levels are high, all of the PAA that is dosed into the evaporator feed stream should precipitate out. The only way in which PAA can be soluble in whey permeate is if it is dosed at a high enough rate so that free calcium is distributed over more PAA molecules. Since these high dosing levels are not practical in an industrial environment it does bring into question how effective PAA really is for this type of application. PAA will drop the level of available calcium for calcium-orthophosphate fouling by forming the calcium-polyphosphate but if hydrolysis is occurring later on in the evaporation then these calcium ions will be liberated back into solution along with orthophosphate ions from the PAA.

All of the results in this and the previous chapter provide evidence that PAA is ineffective as an anti-fouling agent. The fact that only a limited amount of calcium ions can be complexed and also moreover that PAA is prone to hydrolyse, releasing the calcium ions and producing more orthophosphate has lead to the investigation of other possible alternatives to PAA that are discussed in the following chapter.

Chapter 5: Alternatives to PAA

The discovery that PAA precipitates out in whey permeate, rendering it inefficient as an anti-fouling additive, has lead to the investigation also carried out in this project of looking for more effective alternatives for use in the New Zealand Dairy Industry. This investigation includes looking at additives to PAA itself to help enhance its performance and also to investigate possible alternative processing aids. Since the literature of whey permeate anti-fouling additives is scarce the majority of the literature focuses on water treatment and heat exchange water systems.

5.1 Additives to PAA

As an alternative to using purely PAA as an anti-fouling agent, it was proposed that additives could be used to boost its performance. A patent by Bohanon and Geirsch (Bohanon & Giersch, 2000) was found to use industrial sodium hexametaphosphate in conjunction with tetra-sodium or tetra-potassium pyrophosphate as a scale inhibitor for lactose evaporators. It is unsure as to why the pyrophosphate was added so an experiment was conducted to see if the addition has an effect on the calcium tolerance.

Experimental: This experiment was conducted on the same premise as previous calcium tolerance experiments. Three PAA solutions were made up, two contained tetra-sodium pyrophosphate in amounts described by Bohanon and Geirsch. The amounts were on a weight ratio of 19:1 and 4.6:1 of PAA:Na Pyrophosphate.

Results: The patent gives two antifouling formulations that are claimed to help reduce scale build up. One has a polyphosphate to pyrophosphate ratio of 19:1 and the other has a ratio of 4.6:1. These ratios were made up in the present study

and tested for Ca tolerance using the methodology developed in the last chapter. The results are shown in Figure 5-1.

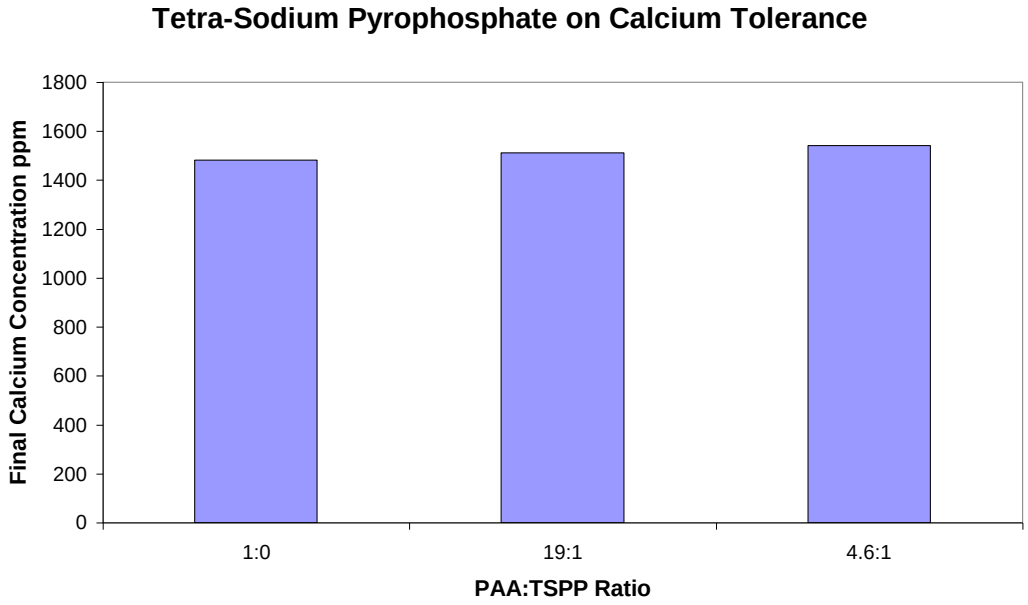


Figure 5-1: Effect of TSPP on PAA calcium tolerance

The graph gives evidence that there is a slight increase in tolerance but compared to the control with no pyrophosphate, the tolerance increase appears marginal. This may suggest that the pyrophosphate may have a different role rather than acting as a solubility support for the polyphosphate. The patent refers to the formula with a ratio of 19:1 as being better than the 4.6:1 mixture.

The pyrophosphate may not act in inhibiting the precipitation of calcium polyphosphate but it does give rise to the possibility that other additives could be used to perform in this way. Although the role of pyrophosphate is not specified in the patent its addition could be for other reasons. It has been shown that pyrophosphates are used as emulsifying agents for proteins (Mizuno & Lucey, 2007). This could be the reason that the pyrophosphate is added because whey permeate can sometimes contain low amounts of proteins if the ultrafiltration step is not performed correctly or the membranes are aged or worn.

5.2 Use of Other Polymers

It was decided that alternative additives needed to be sourced that could replace PAA. A search of current anti-fouling additives that are used in other processing systems were polyacrylic acid, polymaleic acid, carboxymethyl inulin and 1-hydroxyethylidene-1,1,-diphosphonic acid (HEDP). It would be beneficial to look at the properties of these additives to see if they are more efficient than PAA. One of the major obstacles is that the additive must meet New Zealand food safety standards. Food safety was the most important factor and relates to whether the substance can be used in the evaporator and whether it is safe for it to have direct contact with the product. If an alternative additive is more efficient than PAA it may not be able to be used due to its toxicity so there must ultimately be a compromise as to which anti-fouling agent is best to use.

5.2.1 Characterisation of New Inhibitors

An investigation into finding an alternative to PAA resulted in the discovery of other anti-scale inhibitors that are used in the water and sugar industries. Three products have been found that would be viable to use in lactose manufacturing. These products had to fit certain criteria before they could be considered for the use in permeate evaporators. They had to be heat stable at 70°C under vacuum, food safe as they were in direct contact with the final product and needed preferably to be soluble at high concentrations of calcium or have a higher calcium tolerance than PAA.

The first inhibitor found was polymaleic acid (PMA). This is used in the sugar industry when evaporation is needed to concentrate sugar beet solution and also in desalination systems (Doherty *et al.*, 1996; Ralston *et al.*, 1984). A 250 mL sample was received from Scion, Rotorua. Another inhibitor found was carboxymethyl inulin (CMI). This is a fairly new inhibitor and was discovered through the literature (Verraest *et al.*, 1996). Carboxymethyl inulin appears to have the advantage of having a very high calcium tolerance, which is explained later in this chapter. Another advantage of CMI is that it is a “green inhibitor”

being more environmentally friendly due to the fact that inulin in a natural plant extract and is biodegradable.

During the process of gathering samples, a company was found that supplies CMI on an industrial scale. Thermphos is a company that supply calcium scale inhibitors to businesses that use recirculated and potable water systems. They also have another product that has proven very effective against $CaCO_3$ build up, which is a diphosphonic acid. 1-Hydroxyethylidene-1,1-diphosphonc acid or HEDP is used to control calcite crystal growth on heat exchange surfaces. HEDP is very heat stable because of the P – C bond which is thermodynamically stronger than the PAA P – O bond (Koay & Choo, 2008).

5.2.1.1 Preliminary Calcium Tolerance Experiment

Calcium tolerance was used as a measure of effectiveness for the alternative anti-fouling agents. From the three samples that were received, PMA, CMI and HEDP, a preliminary study was carried out to eliminate any additive with obvious poor calcium tolerance.

Experiment: Three 100 mL solutions of 250 ppm $CaCl_2$ were used. To these three solutions, ~5 mL of 100 ppm of inhibitor was added drop-wise to each via a plastic pipette and the experiment stopped when a precipitation was observed or until all the inhibitor was added.

Results: Out of the three alternatives to PAA, one was found to form a precipitate with calcium ions. HEDP showed poor calcium tolerance but this has been demonstrated previously by Amjad (Amjad, 1989). To investigate this precipitate in greater detail the solid was isolated by decanting off the liquid and drying in a 60°C overnight. The dried solid was then pressed into a KBr disk and studied using IR analysis. The resulting spectrum is given in Figure 5-2.

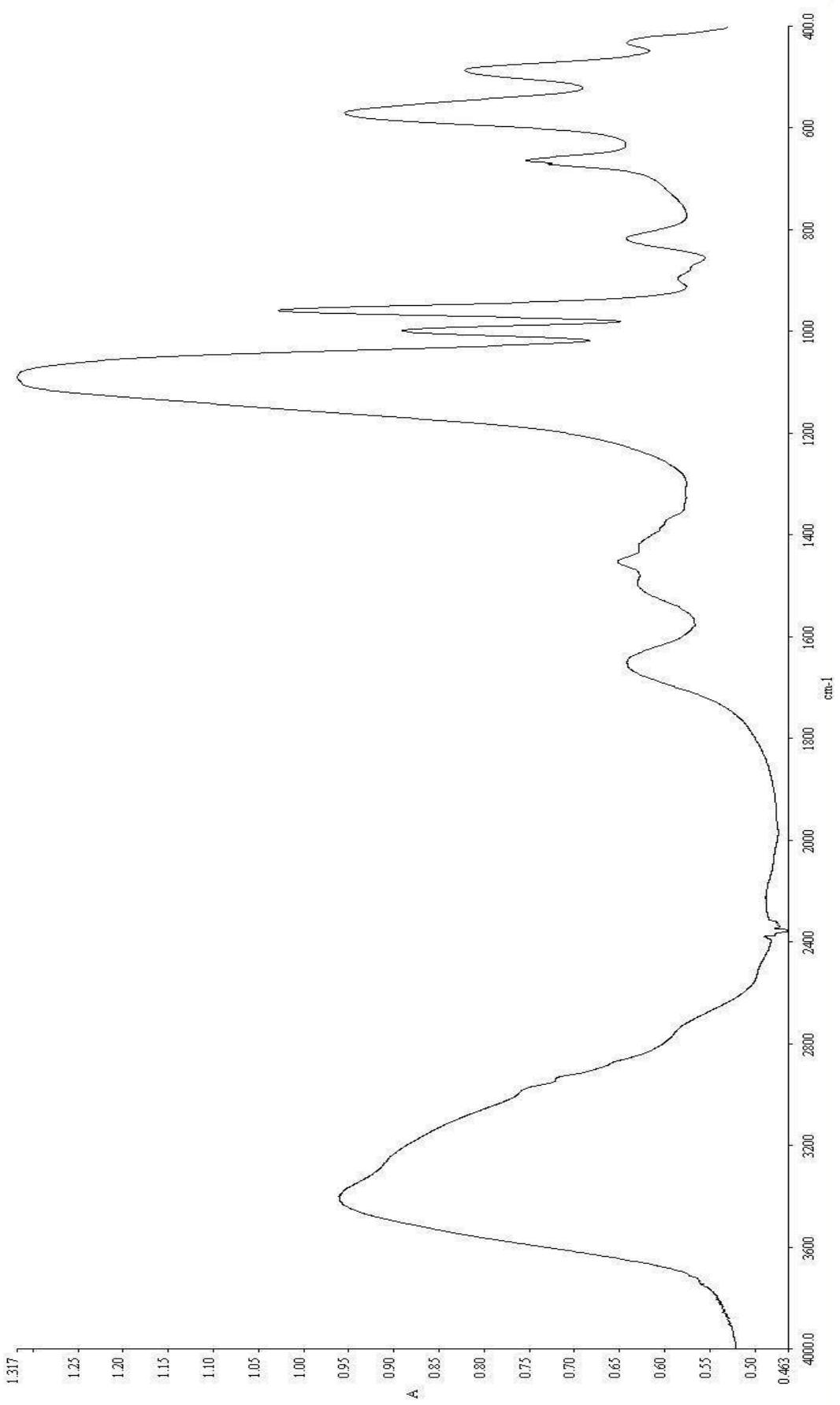


Figure 5-2: IR spectrum of Ca-HEDP precipitate

The Ca-HEDP spectrum shows a strong P – O stretching band around 1200 – 1000 cm^{-1} and also a broad O – H stretch at ~3000 cm^{-1}. There is also some P – O bending signals below 800 cm^{-1}.

5.2.2 Appropriate Alternative for a Plant Trial

Since it has been found that PAA precipitates out of whey permeate solution due to the high calcium concentration, a new series of inhibitors has been sought after in order to obtain an improvement in fouling inhibition. It is apparent that CMI and PMA have much higher calcium tolerance as no precipitate was observed when a calcium solution was added to them, which suggests that they will be more effective as an anti-fouling agent. The problem with these inhibitors is that it is difficult to calculate their effectiveness on an industrial scale.

The amount of PAA that is required to keep the calcium in solution for whey permeate far exceeds the current dosing rate of 0.4% w/w. This is not including the fact that whey permeate is heated and evaporated, increasing the calcium concentration in the process. A Fonterra study Burgess (Burgess, 2006), described earlier, showed a similar result in regards to the formation of a precipitate upon the addition of PAA but incorrectly called the precipitation "fouling", when in fact it was most likely calcium polyphosphate instead of calcium orthophosphate, the common substance in mineral fouling. Without proper characterisation of Burgess's precipitate it cannot be conclusively stated.

There is a need to test the effectiveness of these inhibitors on an industrial scale to obtain quantifiable data for the prevention of calcium phosphate precipitation. There have been previous attempts to determine the effectiveness of PAA industrially but their results have been dubious. As mentioned above the Fonterra study by Burgess regarded the calcium polyphosphate as a form of fouling as this is an inaccurate depiction because the main source of fouling is calcium orthophosphate. Another study (Peacock, 2002) attempted to replicate the fouling conditions in a pilot scale evaporator but the fouling that was observed resembled

burnt brown lactose with little to no white scale calcium phosphate build up, which is what is seen in the plant evaporator.

CMI was chosen over PMA for an industrial trial because it can be sourced more readily and also because it is biodegradable which coincides with Fonterra values. CMI was sourced from Thermphos who are a world leader in anti-fouling agents for the desalination industry. They had also advised HEDP be added with CMI as a mixture on an industrial trial even though it has poor calcium tolerance. HEDP was assessed as a proposed alternative to be used for a trial but as this also had poor calcium tolerance it was decided to go ahead with pure CMI.

5.2.3 Proposed Alternatives

5.2.3.1 Carboxymethyl Inulin

CMI is marketed by Thermphos as Dequest PB11620. This is inulin that has been carboxymethylated to reach an active ingredient of 20%. The carboxymethyl groups act to inhibit calcium salts from growing. A paper by Verraest *et al.* in 1996 shows the potential uses of CMI. It outlines the effectiveness of CMI as an inhibitor for calcium carbonate precipitation.

Support for the use of CMI as a processing aid has come from some of the customers of Thermphos. These are overseas customers that use CMI in sugar manufacturing. Royal Cosun Limited, a Netherlands sugar company have been using CMI for almost 10 years.

CMI is made by carboxymethylating inulin. It has the chemical name (IUPAC): inulin, carboxymethyl ether, sodium salt. The structural formula of CMI is illustrated below in Figure 5-3:

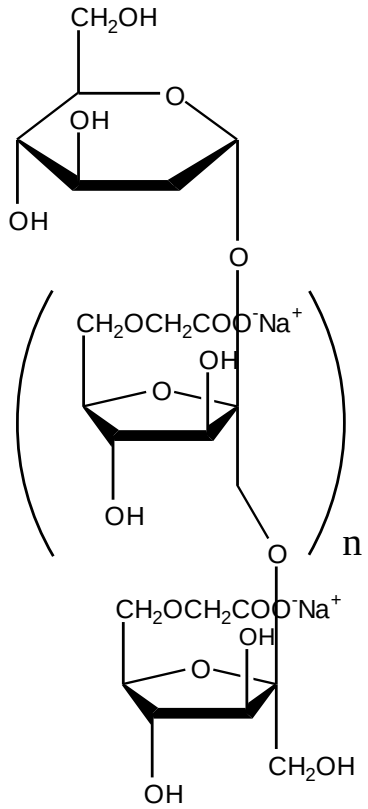


Figure 5-3: Molecular structure of CMI

CMI has an average molecular weight of 2000. The common name and synonym of CMI is sodium carboxymethyl inulin. CMI is marketed as: Dequest PB (Dequest PB 11620 and Dequest PB 11625). The inulin is sourced from chicory roots. This is a renewable feed stock for non-food application. Inulin is marketed by Thermphos as being biodegradable and non-toxic.

Carboxymethyl inulin is used in detergents including automatic dishwashing in Europe and North America. It is also used in pulp & paper production where it is suitable for production of food contact paper and paper board. This compound is also used in water treatment and in oil recovery facilities (including in Norway where it meets most stringent regulation on environmental toxicity). Finally, carboxymethyl inulin is used in the Netherlands as scale inhibitor in both reverse osmosis and nanofiltration process for production of potable water.

Thermphos PB11620 or CMI 20 is a synthesised polysaccharide. It is derived from inulin sourced from Chicory roots. The inulin is carboxymethylated

providing binding sites for calcium. This is prepared via inulin, which is the polysaccharide, reacting with carboxymethyl groups to a degree of substitution of 20%, which it is at a level where it is able to bind calcium ions. This results in the final product known as Carboxymethyl Inulin (CMI 20).

As it was seen in this project, CMI 20 had very good calcium tolerance with no observed precipitate seen. This was also supported by Thermphos who have also supplied evidence to the excellent calcium tolerance. Figure 5-4 shows that lack of turbidity when a calcium carbonate solution is added to CMI 20, where as others such as Dequest 2000, which is a phosphonate similar to HEDP, forms a turbid solution.

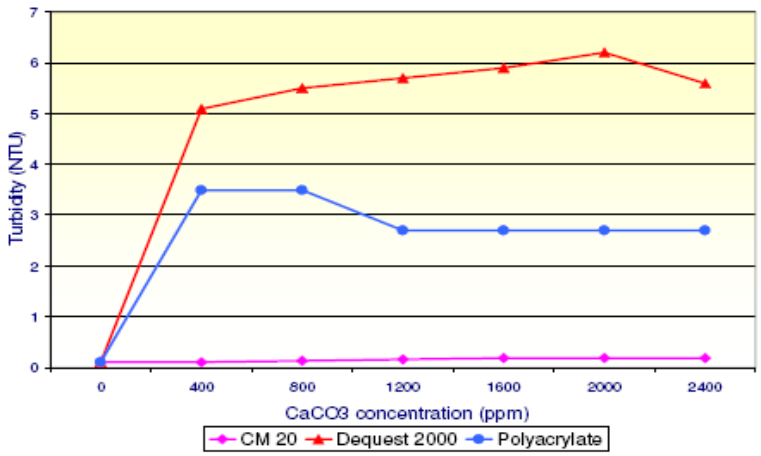


Figure 5-4: Thermphos presentation slide of calcium tolerance of processing aids showing CMI

The main interest in this scale inhibitor is its very high calcium tolerance (demonstrated in Figure 5-4). This is one of the main justifications as to why this alternative should perform better than PAA. The recommended dosing rate of CMI 20 is 200-500 ppm active (or 1000-2500 ppm total) by weight, which is an 8 fold decrease in active ingredient on the current PAA dosing rate of 4000 ppm giving further validation to this change.

5.2.3.2 1-Hydroxyethylidene -1,1,-diphosphonic acid (HEDP)

Dequest 2010 is based on Thermphos ethylidene (1,1-diphosphonic acid) or HEDP and is FDA approved for application in which boiling steam comes in

contact with food. It is noted for its heat stability. HEDP has a P–C bond compared to PAA, which has a P–O. The phosphorus carbon bond is much stronger and will withstand harsh conditions better then the phosphorus oxygen bond which is prone to heat induced hydrolysis.

HEDP does however have poor calcium tolerance much like PAA. It is advised that HEDP be added to the permeate stream as a blend with CMI 20 to help CMI 20 act as a dispersion agent but for the scope of this proposed trial it has been decided to omit HEDP altogether to see if CMI 20 can perform on its own.

5.3 Implementation into Industry

It was anticipated that a trial of CMI 20 could be conducted before the conclusion of this project's duration, but due to unexpected reliability in milk in the Waikato region and bureaucracy, the commencement of this trial has been extended to past the completion date of this thesis. What is discussed from this point is the work that has gone into setting up a trial and the economic viability of such a change in a process, which is an important aspect of conducting and industrial technology project.

As part of an industrial thesis it is important to focus on the economic benefits that arise from this type of research. In this section, focus is shifted away from the laboratory results and moved towards the setting up and implementation of a trial to test the anti-fouling effects of CMI in a whey permeate evaporator. It was hoped that at the completion of this project a successful trial would have been carried out but as it will be discussed there have been many unforeseen delays that have postponed the trial. Most notably the duration it took for CMI to arrive in the country and the need to acquire Food Safety Australia New Zealand (FSANZ) approval for a product that is food safe in other European countries.

5.3.1 Approval Process for Carboxymethyl Inulin

Although CMI is approved for use in other countries as a food contact processing aid, since it is new to New Zealand it has to gain FSANZ approval. This section describes the process that has been taken to get CMI approved for the use in whey permeate evaporators. In search for a new inhibitor to replace that of PAA, a literature search came up with CMI as a new type of mineral scale inhibitor.

To ensure that it had previously been used and was safe, a literature search was carried out to profile its toxicology and other uses. A Toxicological profile that was carried out in 2003 (Johannsen, 2003) on CMI concluded that the results obtained in his study with CMI are consistent with similar data derived on numerous dietary carbohydrate fibres generally recognized as safe in the human diet. The dietary carbohydrate fibres he was referring to was carboxymethyl cellulose, which is a common approved food additive.

A study of crystal growth on calcium oxalate in 2008 (Akin *et al.*, 2008) also mentioned that the results of these toxicity studies with CMI, all conforming to internationally accepted testing standards, show that the toxicological profile of CMI is consistent with other polycarboxylates used in foods, also referencing to carboxymethyl cellulose.

CMI has been supplied to Fonterra for a trial by Thermphos. They market CMI as "Dequest PB11620" and promote it as a food safe product mainly for the European sugar industry. A patent has also been found to promote CMI in the sugar industry (Berends & Kuzee, 1999).

CMI has been used in the sugar industry for almost 10 years. Recommendations from clients of Thermphos have been provided for further assurance. A reference from Royal Cosun Limited, a European sugar company in the Netherlands, has been provided to Fonterra for the use of CMI in sugar juice evaporators.

Since CMI is new to New Zealand it has been advised that an independent study was carried out to ensure CMI's safety. AsureQuality Limited was employed to

carry out the safety report. Carboxymethyl inulin, as the name suggests, is inulin, which is known to be food safe, that has been carboxymethylated. The carboxymethylation process allows the inulin to bind to calcium ions. Inulin is similar to cellulose, another well known food additive. NZFSA has approved the use of Carboxymethyl Cellulose (CMC), giving further support of the approval of CMI.

5.3.2 Financial Analysis of the use of CMI in Whey Permeate Evaporators

For implicating a successful trial for a new alternative to PAA it not only has to work effectively but it also needs to be economically beneficial. It is therefore valuable to do a cost benefit analysis of CMI in comparison to PAA. The assumptions are made from getting the same performance out of the plant but only taking into account the recommended dosing rate.

For PAA the recommended dosing rate is 4000 ppm by weight and for CMI, the recommended dosing rate is 200 ppm active. The current scenario is that 1000 L of CMI has received which is enough to carry out a five day trial. The overall cost benefit of CMI over PAA could possibly result in over $1.5 million dollars in savings.

The dosing rates and the hourly rate of PAA and CMI 20 are given in Tables 5-1 and 5-2 respectively. It highlights the cost effectiveness of CMI 20 compared to PAA. The bold dosing rate denotes the recommended dosing rate (RDR).
Currently PAA is dosed at 4000ppm resulting in a running cost of $123.66/hr.

Recommended dosing rates of CMI 20 are 100-500ppm. CMI 20 dosing rate would have to be 644pm before CMI 20 is equivalent to PAA in terms of chemical cost.

Table 5-1: Running cost of PAA (bold denotes RDR)

PAA	$ 2,290.00	1000L Bulk	as at 12/05/09
	$ 2.29	$/L	
Dosing Rate	Dosing Rate	Usage Rate	Cost Rate
% dry basis	ppm	L/hr	Cost/hr
0.10%	1000	13.50	$ 30.92
0.15%	1500	20.25	$ 46.37
0.20%	2000	27.00	$ 61.83
0.25%	2500	33.75	$ 77.29
0.30%	3000	40.50	$ 92.75
0.35%	3500	47.25	$ 108.20
0.40%	**4000**	**54.00**	**$ 123.66**
0.45%	4500	60.75	$ 139.12
0.50%	5000	67.50	$ 154.58

Table 5-2: Running cost of CMI (bold denotes RDR)

CMI 20	$ 6,950.00	1000L Pod	as at 12/05/08
	$ 6.95	$/L	
Dosing Rate	Dosing Rate	Usage Rate	Cost Rate
% dry basis	ppm	L/hr	Cost/hr
0.010%	100	2.76	$ 19.22
0.015%	150	4.15	$ 28.82
0.020%	**200**	**5.53**	**$ 38.43**
0.025%	250	6.91	$ 48.04
0.030%	300	8.29	$ 57.65
0.035%	350	9.68	$ 67.25
0.040%	400	11.06	$ 76.86
0.045%	450	12.44	$ 86.47
0.050%	500	13.82	$ 96.08
0.055%	550	15.21	$ 105.68
0.060%	600	16.59	$ 115.29

A dosing rate of 200ppm represents a process aid cost reduction of 68.9% which equates to estimated savings of $1545770 $NZ/yr based on site wide usage of 979639L PAA for the financial year of 2009. The projected figures of PAA use for the 2009/2010 season is given in Table 5-3 showing the volumes of PAA that is expected to be used.

There is expected capacity to be gained by spending more time on product if there is less fouling build-up. It is also possible that there will be a reduction in CIP chemical usage per CIP as fouling will not necessarily be the main cause of the plant coming off product and therefore it is envisaged that equipment will not be as badly fouled as the evaporators currently are. If fouling is not the reason for the evaporator to stop then it would either be, if there is a lack of whey permeate or for sanitary reasons to prevent the build up of microbial bacteria.

Table 5-3: Projected volume of PAA to be used in the 09/10 season

Month 2009	**Jun**	**Jul**	**Aug**	**Sept**	**Oct**	**Nov**	**Dec**
Lichfield	10		4500	22631	22876	18643	9171
Clandeboye			37400	65045	48241	50357	43500
Edgecumbe		2000		3023	8062	14612	8062
Hautapu		5800	14700	26423	43938	30535	41016
Morrinsville			1000				
Stirling			26200	9070	17364	29426	5543
Total		**7800**	**83800**	**126192**	**140481**	**143574**	**107291**

Month 2010	**Jan**	**Feb**	**Mar**	**Apr**	**May**
Lichfield	9876	16326	17031	4000	
Clandeboye	65500	46457	4434	12000	13000
Edgecumbe	3023		16023		
Hautapu	36581	31140	38496	2000	2000
Morrinsville					
Stirling	15116	23643	14109	4800	5000
Total	**130097**	**117566**	**90093**	**22800**	**20000**

5.4 Plant Trial of CMI

Lab scale testing can only represent a basic overview of how these products would perform on an industrial scale. Implementing these on a trial basis would be the best way to test their effectiveness. It would be advisable to start off with CMI 20 by itself to see if it can perform on its own. It has been recommended from the manufacturer of these products to have a blend of 1:4 active HEDP:CMI 20. This however may not be the best method as the HEDP has a poor calcium tolerance and will precipitate out. If HEDP does precipitate out however, it will be more stable and will not hydrolyse as readily as PAA due to a thermodynamically stronger P – C bond in HEDP.

It will be best to run CMI 20 for the majority of the trial at 500ppm active. Since CMI 20 is 20% active (hence the "20") this equates to 0.25% w/w compared to PAA 0.4%w/w. This can later be optimised with further refinement if successful.

5.4.1 Trial Objectives

The most obvious and main objective for this proposed trial is centred around the anti-fouling abilities of CMI 20. It is not only important that CMI 20 works as an anti-fouling agent but it must outperform PAA either based on performance as an inhibitor or be economically cheaper to achieve the same performance.

Initially for the trial it will be based on the ability of CMI 20 to perform at the recommended dosing rate but the trial is expected to take a maximum of five days so there is some time in the trial to adjust the dosing rates to find optimal rates of inhibition and also to see if a reduction in the recommended rate will provide the same amount of fouling reduction. Once an appropriate dosing rate has been decided on, this value will then be compared to PAA to see if is financially viable to make the change to a new processing aid.

5.4.2 Performance Measurements

To determine if CMI 20 is effective at reducing calcium fouling, several evaporator process variables can be monitored and compared to those of a PAA run at equal time points. These include:

- The amount of water evaporated for a given amount of steam imputed into the system.
- Total density of exit solids at a given time in a run.
- The amount of vacuum required to maintain the correct evaporation rate which can be attributed to the power output of the MVR recycling fans, which was discussed in Chapter 2.

Monitoring these variables negates the need to observe full runs and also means that all runs can be compared, not only the runs that end due to fouling. Measurements can be taken at specific times throughout the run which can then be compared to one another to see how the rate of fouling is increasing.

It needs to be highlighted that not all runs are the same. There are many variables that exist which need to be considered prior to the trial commencing. These include:

- The steam flow rate / mass flow, which is controlled by the operator but is usually set at the beginning of a run.
- The feed composition is in regards to total solids, ash, lactose and protein levels.
- The source of the whey permeate, whether it is sweet whey or acid whey.
- The feed total solids, which can sometimes fluctuate depending on the total solids that exit the RO.
- The feed pH can also be varied depending on the type of whey permeate and can also fluctuate seasonally. The pH is sometimes lowered manually in the RO process prior to primary evaporation by the use of citric acid.

5.4.3 Proposed Trial Runs

For the trial runs 1000L of CMI 20 has been purchased. This volume is expected to last for at least five 20 hour runs. The proposed starting point of CMI 20 is 200 ppm. This equates to a dosing rate of 5.53 L/hr. This will later be increased to 500 ppm for most of the runs and then an increase up to 1000 ppm for the last run is proposed to see the benefits of a higher dosing rate.

For the trial the existing dosing pump that currently doses PAA will be used, which is a positive displacement pump. This pump will need to be manually tuned down to allow for the lower volumes. The set-up of the trial should take a day to complete with the attaching of the 1000 L pod to the pump. The next five days will be used to conduct the trial. Ideally a control should be conducted that uses no processing aid but since it is being conducted on an industrial scale it is not economically viable to run a no processing aid control.

5.4.4 Post Trial Plans

If the trial is successful then the dosing rate of CMI 20 will be optimised and the possibility of rolling this out for other sites. The main objective is to achieve longer run times so to reduce the amount of product down time running CIP's. If there is a significant extension in run times then it can be determined if CMI 20 will become a permanent replacement for PAA.

If CMI 20 proves unsuccessful then there is the possibility of approaching the fouling problem in a different way. Precipitating out the calcium and extracting it before reaching the evaporator is another consideration that may reduce fouling. This is a possibility that will be considered once the result of this proposed trial has been obtained.

Chapter 6: Conclusion and Recommendations

Over the course of the project is there were findings and difficulties that resulted in the deviation from initial objectives and evolution of new objectives. The difficulty of direct analysis of whey permeate led to valuable learning experiences which ultimately resulted in some knowledge regarding the fate of PAA in whey permeate once it was added. Finding a relevant relationship between laboratory work and applying it on a large industrial scale can be challenging. The move towards consideration of sequestering additives alternative to PAA has become one of the most important aspects of this project in terms of its value to Fonterra.

Matrix effects have proven challenging when working with whey permeate and also inter-instrumental techniques proved to be another problem. This learning experience caused the project to be altered in terms of desired outcomes. The finding of PAA precipitating out of a calcium ion solution was an unexpected revelation in the scope of the work carried out. This led to a better understanding of the chemistry of PAA and its interaction with whey permeate and may also possibly provide an impetus for this additive's eventual discontinued use.

It can be concluded that PAA is most likely an inefficient inhibitor with respect to mineral fouling in whey permeate evaporators because of a misunderstanding in how it is expected to work in the permeate. The low calcium tolerance of PAA means that it probably precipitates out of solution with calcium ions from the permeate rather than staying in solution and remaining as a dissolved sequestrant. This may initially prevent orthophosphate form forming scale build up by reducing the calcium ion concentration but it does not remove all of the calcium at the current dosing levels. For PAA to be effective and to remain in solution, the dosing levels need to be far higher than they currently are but this is not economically viable.

The discovery that PAA has the tendency to break down in boiling water also provides further evidence that PAA is not sufficiently thermally robust to be a

sequestrant at the relatively high operating temperatures of the evaporation plant. Boiling a solution of PAA causes an increase in the amount or orthophosphate. Whey permeate is under vacuum and at a temperature above 65°C, all conditions which may cause the breakdown of PAA releasing the calcium ions back into the system but then also creating further orthophosphate ion available for mineral fouling. Further investigation will need to be carried out to justify these claims though some evidence has been provided via calcium tolerance experiments.

Investigation into other anti-fouling agents resulted in the selection of carboxymethyl inulin as a possible replacement of PAA. A few were proposed and a selection was sourced to run laboratory tests. Calcium tolerance was the main bench mark for anti-fouling efficiency. HEDP was found to be inefficient as it had poor calcium tolerance much like PAA. PMA and CMI meet the criteria that were set out in this project. PMA and CMI both reportedly have excellent calcium tolerance but CMI was chosen due to its commercial availability and lower cost. The problem that remains for the use of CMI in whey permeate evaporators is getting food safety approval in New Zealand.

CMI is currently used in Europe as a scale inhibitor in sugar juice evaporators. It is recommended that a trial be carried on an industrial scale to see if CMI is an effective anti-fouling agent in whey permeate evaporators. At the conclusion of this project 1000L of CMI has been delivered but a trial date is still waiting to be confirmed.

Although PAA is reported to help give longer runtimes for the evaporation of whey permeate, the way in which it provides this is suspected to be via a simple lowering of the calcium ion by straight precipitation which is not reasoned to be very suitable from an economic viewpoint. It is important to look at improving current technologies and ideas in the industry where advancements have been made. The use of CMI should be seriously considered as a cheaper and possibly more effective replacement which would provide a more authentically sequestrant role than PAA.

Appendix A: Calculation of Reynolds Number for Rig #2

Below are the calculations that were used for the design scope of the second fouling rig. The Reynolds number was important to calculate as turbulence would have affected the type of fouling adhesion and also would provide a different environment to that of a falling film evaporator.

Equation A-1: Reynolds number equation

$$\text{Reynolds Number} = \frac{\rho V D}{\mu}$$

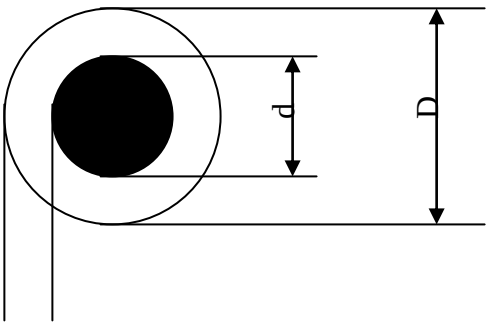
ρ = Density = 1200 kg/m^3

V = velocity (m/s)

μ = Viscosity = 0.01cP = 10 P = 10 kg/ms

D = Distance/Diameter (m)

For the gap the whey will travel through (assume 5mm):



5 mm Gap

$$\text{Cross Sectional Area} = \pi\left(\frac{D-d}{2}\right)^2 m^2$$

D – d = 10mm = 0.01 m

$\left(\frac{D-d}{2}\right)^2$ = 0.0001 m

Flow rate = 1.3 L/min

$$V = \frac{1.3L}{\min} x \frac{1m^3}{1000L} x \frac{1\min}{60\sec} x \frac{1}{0.0001\pi m^2} = 0.2167 m/\sec$$

If we assume a Reynolds Number of 2000 for laminar flow:

$$D = \frac{2000\mu}{\rho V}$$

= 2000x10(kg/ms) / 1200(kg/m^3) x 0.2167(m/s)

= 3.61m = Distance/Diameter

Appendix B: Calculation of a 0.001 mol L^{-1} Ca^{2+} Stock Solution with an Ionic Strength of 0.1 mol L^{-1}

The dissolving of calcium carbonate with hydrochloric acid gives the following equation:

Equation B-1: Neutralisation of calcium carbonate

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_{2(g)}$$

For a 1 litre volume of stock solution a known amount of 4 mol L^{-1} KCL solution needed to be added for create an ionic strength of 0.1 mol L^{-1}. Using the equation:

Equation B-2: Total ionic strength of a solution

$$I = \frac{1}{2}\sum C_i \, z_i^2$$

Where I is the total ionic strength, C is the concentration of a given ion and z is the charge of that ion. Therefore a volume of 4 mol L^{-1} KCL, known as x, has to be added to the 1 L solution to make up ionic strength.

$$I = \frac{1}{2}([Ca^{2+}]\times 2^2 + [Cl^+]\times 1^2 + \frac{x\,(Volume\ of\ KCl)}{1000\,(Final\ volume)}\times 1^2 \times 2\,(Cl^+ + K^+)\times 4\,(mol))$$

$$I = \frac{1}{2}(0.001\times 2^2 + 0.002\times 1^2 + \frac{x}{1000}\times 1^2 \times 2 \times 4)$$

$$I = 0.1$$

$$0.1 = \frac{1}{2}(0.006 + \frac{8x}{1000})$$

$$\frac{8x}{1000} = 0.2 - 0.006$$

$$8x = 194$$

$$x = 24.25\,mL\ of\ 4\,mol\ L^{-1}\ KCl$$

References

Akin, B., Oner, M., Bayram, Y., & Demadis, K. D. (2008). Effects of Carboxylate-Modified, "Green" Inulin Biopolymers on the Crystal Growth of Calcium Oxalate. *Crystal Growth & Design, 8*(6), 1997-2005.

Amjad, Z. Scale Inhibition in Desalination Applications: An Overview. *The NACE International Annual Conference and Exposition*.

Amjad, Z. (1989). Effect of Precipitation Inhibitors on Calcium Phosphate Scale Formation. *Canadian Journal of Chemistry, 67*(5), 850-856.

Amjad, Z. (1998). *Calcium Phosphates in Bioloical and Industrial Systems*: Kluwer Academic Publishers.

Amjad, Z., Zuhl, R. W., & Zibrida, J. F. (2003). Factors Influencing the Precipitation of Calcium-Inhibitor Salts in Industrial Water Systems. *Association of Water Technologies, Inc. 2003 Annual Convention*.

Bansal, B., & Chen, X. D. (2006). A Critical Review of Milk Fouling in Heat Exchangers. *Comprehensive Reviews in Food Science and Food Safety, 5*(2), 27-33.

Berends, R., & Kuzee, H. C. (1999). Process for Controlling Scale in the Sugar Process. In E. P. EP1060135 (Ed.).

Bohanon, L., & Giersch, G. J. (2000). Compositions and method of treatment of whey. In U. Patent (Ed.). United States of America.

Bott, T. R. (1995). *Fouling of heat exchangers; Chemical Engineering Monographs, # 26*: Elsivier Science B. V. Amsterdam.

Burgess, G. (2006). *Process Aid "A" Optimisation Project*, Fonterra.

Chui, G. (2007). Optimisation of PAA. Fonterra.

Daufin, G., Labbe, J. P., Quemerais, A., Brule, G., Michel, F., Roifnant, M., et al. (1987). Fouling of a heat exchange surface by whey, milk and model fluids. An analytical study. *Le Lait, 67*(3), 339-364.

de Jong, P. (1997). Impact and control of fouling in milk processing. *Trends in Food Science & Technology, 8*(12), 401-405.

Doherty, W. S., Crees, L., & Senogles, E. (1996). Polymeric Additives : Effects on Crystallization of Hydroxyapatite Scales. *Cryst. Res. Technol., 31*(3), 281-286.

Eaton, A. D., Franson, M. A. H., & Clesceri, L. S. (2005). *Standard methods for the examination of water & wastewater*.

Fonterra. (2009). *http://www.fonterra.com/wps/wcm/connect/fonterracom /fonterra.com/our+business/fonterra+at+a+glance/about+us/key+facts*: Fonterra Co-operative Group.

Johannsen, F. R. (2003). Toxicological profile of carboxymethyl inulin. *Food and Chemical Toxicology, 41*(1), 49-59.

Jun, S., & Puri, V. M. (2005). Fouling Models for Heat Exchangers in Dairy Processing: A Review. *Journal of Food Process Engineering, 28*(1), 1-34.

Koay, C. H. E., & Choo, S. (2008). Superior thermal Stability of HEDP over SHMP.

Lin, M.-J., Lewis, M. J., & Grandison, A. S. (2006). Measurement of ionic calcium in milk. *International Journal of Dairy Technology, 59*(3), 192-199.

Mizuno, R., & Lucey, J. A. (2007). Properties of Milk Protein Gels Formed by Phosphates. *Journal of Dairy Science, 90*(10), 4524-4431.

Morison, K. R., & Tie, S. H. (2002). The Development and Investigation of a Model Milk Mineral Fouling Solution. *Food and Bioproducts Processing, 80*(4), 326-331.

Odagiru, S., & Nickersion, T. A. (1964). Complexing of Calcium by Hexametaphosphate, Oxalate, Citrate, and EDTA, in Milk. I Effects of Cimplexing Agents on Turbidit and Rennet Coagulation.

Ozrenk, E., & Inci, S. S. (2008). The Effect of Seasonal Variation on the Composition of Cow Milk in Van Province. *Pakistan Journal of Nutrition, 7*(1), 161-164.

Packer, J. E., Robertson, J., & Wansbrough, H. (1998). *Chemical Processes in New Zealand* (2 ed. Vol. 1): Expo Digital Documents Centres Ltd.

Panova, N. N. (2001). *Calcium Phosphate Precipitation from Whey Permeate.* University of Waikato.

Peacock, L. (2004). *Whey Permeate Evaporator Fouling.* Massey University.

Prakash, S., Datta, N., & Deeth, H. C. (2005). Methods of Detecting Fouling caused by Heating of Milk. *Food Reviews International, 21*, 267–293.

Ralston, P. H., Whitney, S. L., & Walker, J. L. (1984). Control of Scale in Sugar Evaporation Equipment. In U. S. Patent (Ed.): Calgon Corporation.

Ramachandra, S. S., Wiehe, S., Hyland, M. M., Chen, X. D., & Bansal, a. B. (2005). A Preliminary Study of the Effect of Surface Coating on the Inital Deposition Mechanisms of Dairy Fouling. *ECI Symposium Series, RP2:*.

Rashchi, F., & Finch, J. A. (2000). Polyphosphates: A review their chemistry and application with particular reference to mineral processing. *Minerals Engineering, 13*(10-11), 1019-1035.

Reithel, F. J., & Venkataraman, R. (1956). Lactose in the Sapotaceae. *Science, 123*(3207), 1083 - 1084.

Rosmaninho, R., Santos, O., Nylander, T., Paulsson, M., Beuf, M., Benezech, T., et al. (2007). Modified stainless steel surfaces targeted to reduce fouling - Evaluation of fouling by milk components. *Journal of Food Engineering, 80*(4), 1176-1187.

Santos, O., Nylander, T., Paulsson, M., & Tragardh, C. (2006). Whey protein adsorption onto steel surfaces--effect of temperature, flow rate, residence time and aggregation. *Journal of Food Engineering, 74*(4), 468-483.

Schraml, J. E., & G., K. H. (1996). Effect of Concentration on Fouling of Whey. *Milchwissenschaft, 51*(3).

Simmons, M. J. H., Jayaraman, P., & Fryer, P. J. (2007). The effect of temperature and shear rate upon the aggregation of whey protein and its implications for milk fouling. *Journal of Food Engineering, 79*(2), 517-528.

Takahiro, T., Satoshi, N., & Susumu, A. (1991). Is lactose really present in plants? *Journal of the Science of Food and Agriculture, 54*(2), 305-308.

Thomas, R. (2002). *A Beginner's Guide to ICP-MS*.

ToolBox, T. E. (2005). An introduction and definition of the dimensionless Reynolds Number - with online calculators. *http://www.engineeringtoolbox.com/reynolds-number-d_237.html*.

Verraest, D. L., Peters, J. A., van Bekkum, H., & van Rosmalen, G. M. (1996). Carboxymethyl Inulin: A New Inhibitor for Calcium Carbonate Precipitation. *JAOCS, 73*(1), 55-62.

Visser, J., & Jeurnink, T. J. M. (1997). Fouling of heat exchangers in the dairy industry. *Experimental Thermal and Fluid Science, 14*(4), 407-424.

Zhou, W., & Wang, Z. L. (2007). *Scanning microscopy for nanotechnology: techniques and applications*: Springer.