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Chemical cleaning of starch based deposits from hard surfaces

Din, Rizwan

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CHEMICAL CLEANING OF STARCH BASED DEPOSITS FROM HARD SURFACES

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Rizwan Din

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

PREFACE

The work described in this thesis has been carried out in the Department of Chemical Engineering, University of Bath, between January 1994 and December 1997. The work is original, except stated in the text. Neither the present thesis, or any part thereof, has been submitted at any other University.

There are a number of people I would like to thank for their help and support throughout the course of my research. I am grateful to my supervisor, Dr Michael Bird for his advice and encouragement.

I also appreciate the financial support from the BBSRC and the technical support provided by the Chemical Engineering Department, especially Merv Newnes who was very helpful in the design and construction of the cleaning rig.

I dedicate this thesis to my father who worked hard all his life so that I would have the chances he never had. Your memory will live on Dad: may Allah's blessings be upon you forever. To my Mum and sister for all the love, encouragement and endless support they have provided throughout all the trials and tribulations we have had to bear. They have given me strength to fight on. My thanks to some special friends who have stuck by me through thick and thin and kept me sane: Harminder, Iggy, Terri, Liz and Crocetta.

SUMMARY

An overview of the chemical cleaning of food based deposits is presented and starch fouling effects are discussed. A literature review of hard surface cleaning, with particular reference to mechanistic and modelling studies is presented since the cleaning of starch based deposits in the Food Industry are commonplace, but the mechanisms involved are not well understood.

The study is divided into two main experimental sections: the first concerns a static cleaning study of modified potato starch deposit removal from stainless steel surfaces using an ultrasonic cleaning bath. The results indicate an optimum concentration of 14wt% for both sodium hydroxide and nitric acid. The existence of temperature optima at 60°C was also found for sodium hydroxide. The other, more detailed investigation involves the study of the cleaning of baked wheat starch deposits from stainless steel surfaces under controlled thermo-hydraulic conditions.

There were a number of novel features built into the design of the flow cleaning rig: it was equipped with a data logging facility to enable continuous monitoring of the parameters affecting cleaning. Two techniques were employed to measure the kinetics of the cleaning process: one measured the starch remaining on the surface (gravimetric) and the other measured the starch contained in the effluent stream using TOC (Total Organic Carbon) measurement. Visualisation of the process was possible in a rectangular-sectioned glass flow cell, enabling the use of video camera-aided recording of the cleaning process. The influence of temperature, velocity and concentration have been identified for a number of aqueous based cleaners. The non-ionic surfactant (alcohol ethoxylate) was found to be the most effective cleaner. Detailed visual removal techniques have provided invaluable information on the mechanisms of removal: it indicated a two stage process of deposit swelling and then subsequent break-up of the fouled layer into discrete aggregates.

Modelling was developed using statistical techniques based on experimental evidence. The model simulations were compared to the experimental results and good agreement was found. Options for future work on hard surface cleaning and process optimisation were proposed.

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Chapter 1: The Cleaning Problem

1.1 CLEANING IN THE FOOD INDUSTRY

Surfaces in contact with product in the food industry require thorough cleaning at regular intervals as a result of deposition of both organic and inorganic soils. This fouling affects both the product quality and safety as well as process operation and control. A major challenge in cleaning is the recognition of residual soil that may resist removal by presently accepted methods of cleaning. The residual soil may nourish micro-organisms that constitute potential health hazards. Insufficient cleaning can also lead to product contamination, causing damage or loss of product. To avoid the loss of profit entailed, continuously operating production plants are submitted to periodic cleaning. Progress in procedures and criteria for evaluating the effectiveness of cleaning has not kept pace with growing complexion of food processing equipment and cleaning processes. Two methods of treatment are commonly adopted in industrial cleaning:

1. **Two Stage** - typically using an alkali such as sodium hydroxide, rinsing with water and followed by treatment with an acid such as nitric or phosphoric acid.
2. **Single Stage** - using formulated detergents containing a cocktail of surfactants and chelating agents.

Although the two stage process may be more complex to employ, the single stage chemicals are generally more expensive but tend to reduce the total cleaning time and cost by a more economical use of water, labour and down-time. In the past, the length of these cleaning intervals has been decided upon an empirical basis. This has been shown in the food industry, particularly the milk industry, by the cleaning tasks in production processes fulfilled by fully automatic **CIP** (Cleaning In Place) systems of high technical standard. There is growing environmental concern due to the generation of large quantities of effluent containing potentially harmful chemical cocktails as a result of the cleaning process (Graβhoff [1989]). Hence, considerable time, detergent and energy might be saved if a clear understanding of the principles involved and a knowledge of the effect of certain variables were determined (Bird and Espig [1994]).

It can be concluded from the literature that the present state of knowledge of cleaning processes is poor and insufficient. This is particularly true for the cleaning mechanisms and kinetics. Recent work has focused more extensively on the mechanisms of fouling rather than cleaning. The main conclusion that has been drawn from this survey is the need to develop a precise method for evaluating the cleaning processes, a prerequisite to predict dynamics with sufficient accuracy to realise process optimisation.

1.2 DEFINITION OF CLEANING

The general definition of cleaning is the removal of unwanted deposit from solid surfaces. This mechanical cleaning is by means of forced convection, induced turbulence or mechanical erosion. Cleaning can be divided into five sub-categories (Sandu et al [1985]):

1. **Dissolution cleaning** - dissolving of a substance by a liquid, leading to the formation of a homogeneous liquid phase.
2. **Dispersion cleaning** - dispersion of the fouled deposit into particles by the action of surfactants.
3. **Chemical reaction cleaning** - solubilisation of the fouled deposit as a result of a chemical reaction with a cleaner.
4. **Surface-polishing cleaning** - the superficial layer on a metal surface is physically removed.
5. **Sanitation cleaning** - removal/ inactivation of microbes attached to a heat exchange surface by the action of thermal/ chemical treatment.

1.3 CLEANING STARCH DEPOSITS

Starch occurs in nature as water-insoluble granules, mainly found in seeds, roots and tubers of green plants. The starch granule is partly crystalline and consists of two major components: amylose and amylopectin. The amylose content can vary over a broad range, but typically amounts to 20-25 wt%. Amylose is a linear (1-4)-linked α-D-glucan and can have a degree of polymerization of up to 600. Amylopectin is the major component of the granule and has a molecular mass between 106 and 108. It is a branched (1-4)-linked α-D-glucan, containing about 5% of (1-6)-linked branch points. The side chains are linear and two main populations are observed: "short" (DP ca.15) and "long" (DP ca.45) chains. The branch points in the amylopectin molecule are clustered, resulting in adjacent linear segments that form thin lamellar crystalline domains. It is this highly-organised structure that determines the unique physicochemical behaviour of starch and makes it such an interesting and versatile material.

In Europe starch is mainly produced from maize, wheat and potatoes. In 1994 the total EU market for starch products amounted to more than 6 million tonnes (Gerts [1996]). Starches are used as native starches, modified starches and as starch hydrolysates, resulting in a wide range of products for food and non-food applications. Important food applications are in the production of processed food, confectionery, food products and beverages. Non-food uses include paper, corrugated board production as well as binders and adhesives.

Many foods contain native or modified starch types which are thermo-sensitive. The processing of starch based products often results in the formation of viscous pastes which can lead to fouling on hard surfaces. The early work based on starch cleaning has been based on textile cleaning (Kling and Lange [1960]). In the food industry, most studies have focused on milk and its products due to the nature of fouling and the simple kinetics that have been deduced as a result of this. However, very little work has been documented on the effective cleaning of carbohydrate soils.

A summary of research on the cleaning of different foodstuffs is given in Table 1.1:

FOODTYPE	RESEARCHERS
Starch	Maruyama et al. [1991], Linderer [1994]
Tomato pastes	Cheow and Jackson [1982]
Chocolate pastes	Schlussler [1970]
Sugar	Rao et al [1993]
Beef Tallow	Tachibana [1960]
Coffee	Takahashi et al. [1997]
Egg Albumin	Ling et al. [1978]
Whipping cream	Maas et al. [1985]
Milk	Bird [1993], Lalande and Rene [1988], Shere [1942]

Table 1.1 Researchers on cleaning of different foodstuffs

The purpose of this dissertation will be to elaborate on the understanding of the mechanisms involved in the cleaning of starch deposits from hard surfaces by means of a systematic experimental study. This will enable the development of kinetic models to describe the cleaning process.

1.4 MECHANISMS INVOLVED IN CLEANING

Jennings [1965], emphasised the importance of energy phenomena involved in the soiling and cleaning processes in his analytical studies. He concluded that sufficient energy needs to be supplied to break the soil-substrate bond in a three phase process of cleaning:

1. Displacing soil from the equipment surface,
2. Dispersing soil in deterging medium and preventing its redeposition,
3. Flushing dispersed soil and detergent out of the equipment.

The majority of energy is expended in the first step. In a flow system, it is caused by friction between deposited soil and fluid flowing past it. This can be expressed in terms of the turbulence of fluid.

On the basis of this analysis, Harper [1972], was the first to explain theoretically that the cleaning mechanism is divided into several steps:

1. Transport of the cleaning solution to the soiled surface,
2. Separation of soil from contact surface by means of wetting and penetration of the soil by the cleaning solution and reaction of the latter with the soil constituents,
3. Dispersion of the soil into the deterging medium,
4. Prevention of soil re-deposition on the surface.

This mechanism can only be related to the experimentally observable cleaning kinetics of a given soil after the parameters affecting cleaning have been identified and their influence on the kinetics isolated. It is very difficult to isolate the second step phenomena: wetting, penetration and reaction between soil components and cleaning products. This explains why this whole mechanism has never been evidenced experimentally. Fundamental studies involving model systems of homogeneous soils on smooth homogeneous surfaces, as in the removal of oily or particulate soil from textile fibres or glass surfaces, have helped gain considerable understanding of the cleaning mechanisms (Paulsson [1989]). However, most food handling equipment involves heterogeneous soil deposits, frequently containing fats, carbohydrates, gummy residues, particles of products such as milk, meat, egg, fruit or vegetable residues.

A pictorial view of the mechanisms involved is provided by Lund et al. [1985] and is shown in Figure 1.1 as the fouling-cleaning cycle. They have divided the cleaning process into six steps which can take place in a cleaning process:

1. Bulk reaction with dissolved or dispersed particles.
2. Transport to the surface by eddy or molecular diffusion.
3. Transport to the fouled layer by capillarity or molecular diffusion.
4. Cleaning reaction (either physico-chemical or chemical).
5. Transport back to the interface by molecular diffusion.
6. Transport to the bulk by molecular diffusion through the boundary layer.

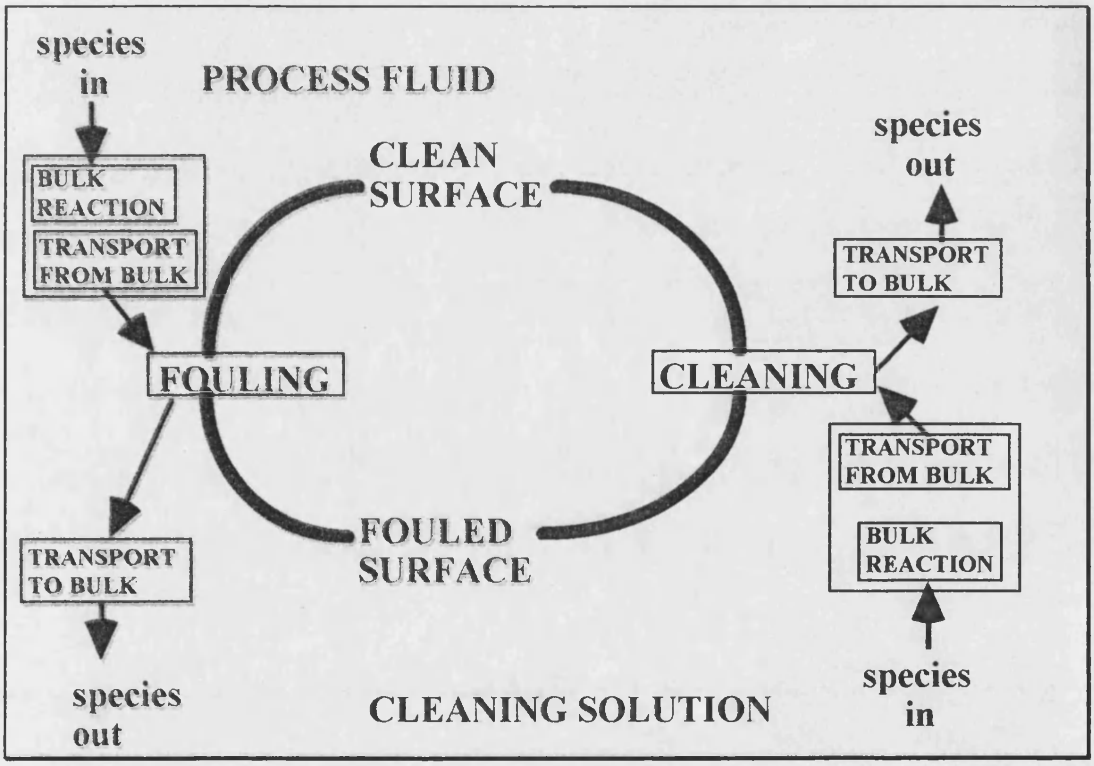


Figure 1.1 Fouling-Cleaning Cycle (after Lund et al. [1985])

Graβhoff [1983] described the cleaning process taking place during the cleaning of heat exchanger surfaces soiled with proteins. He divided the mechanism into three phases although he did not propose a mathematical model for the process:

1. ***Diffusion and swelling stage***. As the cleaning fluid diffuses into the hardened soil, the deposit swells to between two and three times its original thickness.

2. ***Cleaning stage*** where cohesive forces have been weakened to the extent of removal in plaques until a residue of no more than 5% remains.
3. ***Clean surface*** with no deposit when the thin bottom inorganic layer is treated with an acid cleaning solution.

Graβhoff [1983] also proposes that mass transfer of soil particles into the cleaning solution determines the speed of the cleaning process. Stages 2 and 3 have mass transfer of soil particles into the cleaning solution taking place parallel to the decomposition of the soil.

Bird and Fryer [1991] have described the cleaning mechanism by using visual techniques and scanning electron microscopy (SEM) for the removal of whey proteins based deposits from stainless steel surfaces using caustic based cleaners. Their mechanism proposes a three stage removal of proteinaceous matter:

1. Immediate removal of a weak-linked layer of soil on contact with caustic soda. Swelling of the deposit and surface deposit becomes translucent,
2. Surface break up and aggregates enter the bulk flow,
3. After protein removal is complete, a mineral deposit remains on the surface which must be removed by an acid cleaning agent.

Hence this mechanism is governed by mass transfer, diffusion and reaction; each of which could control the rate of the process. All the mechanisms described except by Harper [1972], relate to heat exchangers fouled with proteins. Lund et al [1985] as well as Bird and Fryer [1991] regard cleaning as a heterogeneous process, which is supported by the visual findings of Graβhoff [1983].

1.5 FACTORS AFFECTING CLEANING

In the discussion of the factors affecting cleaning, as reported in the literature, a qualitative comparison is discussed in terms of three basic groups as shown in Figure 1.2. These are mechanical design, operating and system parameters (Goederen [1989]).

1.5.1 Operating Parameters

The influence of operating parameters on cleaning kinetics are important in the optimisation of CIP processes. These parameters not only determine the energy and detergent consumption costs for the operation of the cleaning system, but also the downtimes in the production process to be scheduled for cleaning.

Calbert [1958] discovered that the temperature and hardness of the water in a cleaning solution had an influence on the effectiveness of cleaning. He recommended that during the cleaning cycle the initial temperature of the cleaning solution should be approximately 50-60°C and it should not be allowed to cool to lower than 30°C. Smith and Roth [1972] reported approximately the same temperature range for circulating cleaning solution in pipe-lines. For the more difficult job of cleaning circulating plate heat exchangers, Smith and Roth [1972] used temperatures as high as 90°C.

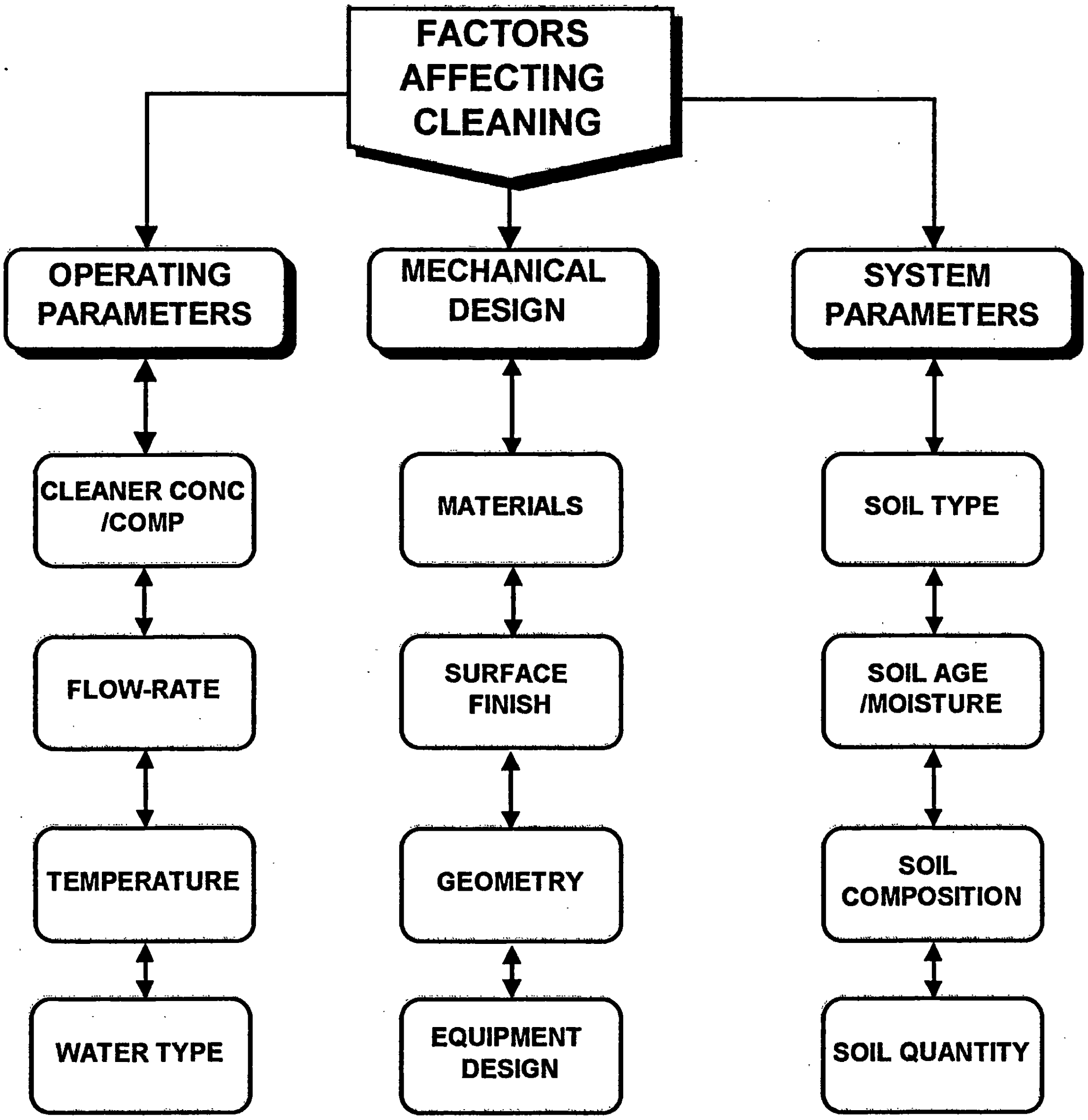


Figure 1.2 Factors involved in process plant cleaning (after Goederen [1989])

The influence of mineral content in water was further investigated by Jennings [1959] and it can be controlled either by the use of an ion-exchange softener or by adding a chelating agent such as ethylenediamine tetracetic acid (EDTA) to the detergent. However, the use of EDTA in Europe is now somewhat limited due to environmental concerns (Graβhoff [1994]).

Jennings et al. [1957] observed that turbulence, as indicated by the Reynolds number, was more important than temperature in cleaning and that both factors became less important as the amount of detergent increased. They found that cleaning effectiveness could be attained at Reynolds Number greater than 25000 and that higher temperature seemed to be slightly more important in the lower turbulence range (Re<25000) range.

Goederen [1989], considers the flow velocity to be the most critical factor on the cleaning effect in HTST and UHT sterilisation processes.

Jennings [1959], also studied effective in-place cleaning and his work identified the role of 5 factors:- contact time, temperature, turbulence, detergent concentration and composition and mineral content of water involved in the cleaning of films of milk. The temperature plays an important role in the cleaning kinetics and is expressed in an Arrhenius rate equation (see Chapter 3). Both the concentration and more importantly, the composition of the detergent, have an effect on cleaning provided it remains in solution. This point is noteworthy in the behaviour of many surfactants which display a "cloud point" temperature above which the surfactant can precipitate out of solution. Jennings also noted that fatty-type soils were not completely and readily soluble in the deterging medium and therefore required special removal mechanisms. Anderson et al. [1969] studied the removal of fat from glass by the solvent action of carbon tetrachloride and found a tightly held layer which resisted removal by solution.

In later work concerning foam formation and air inclusion in the circulating medium, Jennings [1959a] observed that entrained air, by its scrubbing action contributed to the cleaning. However, a build-up of foam caused by air was shown to exert a cushioning effect, acting as a buffer between the solution and surface to be cleaned. He theorised that entrained air could be achieved by positioning the recirculation pump to draw rather than force the cleaning solution through the area to be cleaned. A discussion on foam build-up and its effects on viscosity in the cleaning process is provided by Asher [1975]. He points out that the most important cause of bubble stability and formation is the surface activity (hydrophobic action) of solution. In addition, the collapse of the foam can be brought about by the neutralisation of electrostatic charges on the molecules.

All these authors have studied the cleaning of equipment under conditions approaching commercial operations, and each has reported conditions that will achieve "satisfactory cleaning". However, the information would be more valuable if the minimal conditions necessary to achieve satisfactory cleaning were identified because the influence of individual variables could then be studied.

1.5.2 Mechanical Design

The mechanical design of food equipment influences both capital costs on construction and operational costs due to their effect on the fouling and cleaning dynamics. The nature and conditions of the surface are factors which determine the magnitude of soil-substrate adhesion forces. The corrosion resistance of the construction materials has to be taken into consideration, otherwise the surface properties and conditions will deteriorate with time, producing more active sites for fouling (Bott [1990]). Hence stainless steel has been chosen for this study due to its relative inertness to corrosion by the majority of chemical cleaners.

Several workers have considered the effect of surface roughness on cleaning efficiency. Masurovsky and Jordan [1958], demonstrated that the number of P^{32}-labelled bacteria existing on surfaces after ultrasonic cleaning was affected by the nature of the surface, with Teflon showing least retention with Pyrex, polyethylene and stainless steel showing progressively greater retention. When three degrees of surface finish were investigated, retention was less for highly polished surfaces. Harris et al. [1961], suggested that adsorption and desorption are affected not only by the polarity of the surface but also by the polarity of the adsorbed substance. In related work, Harris [1961] found evidence indicating that nylon, Teflon, methacrylate and stainless steel have relatively few adsorption sites. They showed that the adsorption of C^{14} labelled algal protein, stearic acid and tristearin soils by stainless steel is of an ion-exchange type. These substrates also adsorbed anionic and non-ionic surfactants as well as various sequestering and chelating anions. Such adsorbed materials affected the degree of removal of subsequently applied soil. Pretreatment of a surface with alkali generally increased its adsorption powers more than did an acid pretreatment. Both treatments are believed to increase the adsorption sites for stainless steel.

Harris and Satenek [1961] also found that freshly ground glass exhibited more, adsorptive sites of a less tenacious nature than did stainless steel per unit surface area. They computed this surface area by assuming a monomolecular layer (Anderson et al. [1969]) and calculating the cross-sectional area of an adsorbed C^{14} tristearin molecule. On the basis of the increased adsorption on the ground-glass surface, they calculated that roughening had about doubled the surface area. This suggests that the greater soil retention of the roughened surface may not be entirely due to entrapment of soil in voids and crevices, but at least in part to a physical extension of the surface so that a greater surface area is exposed. For these reasons, a smooth surface finish has been chosen to minimise the mechanical forces of adhesion (see Chapter 2).

1.5.3 System Parameters

This describes the fouling process and its subsequent influence on the cleaning process. Practical applications of starch often consist of gelatinization by heating granular starch in the presence of water. The gelatinization behaviour of starch depends strongly on the amount of water available, processing conditions, characteristic properties of starch and the presence of other components.

Bourne and Jennings [1961] found that the rate of soil removal affected by detergent cleaning was dependent upon the time involved in depositing the soil in a pipe flow system.

Harris [1958] observed that the electrokinetic forces were of considerable importance in the mechanism of soil removal and redeposition. He stated, that in the detergent system it is desirable that the zeta potentials of soil particles and substrate become nearly equal so as to reduce attractive forces which cause them to adhere.

1.6 DETERMINING CLEANABILITY

The concept of cleanliness as applied to the food industry encompasses physical, chemical and biological considerations in the development of criteria for acceptability (Romney [1990]. The removal of visible residues from process surfaces is not an indicator of perfectly cleaned equipment as evidenced by the presence of micro-organisms even after successful circulation cleaning (Bott [1990]). A succession of inadequate cleaning operations can lead to the build-up of a significant soil residue (Hasting [1994]).

Regulatory control guidelines for food processing prescribe that equipment used must be clean prior to use. The term “clean” is taken by food sanitarians to mean "completely free" of soil residues from any preceding use or extraneous contamination. However, the term "relatively clean" may be a more appropriate description of the actual conditions experienced in the majority of food processing equipment (Harper [1972]).

A number of workers have used the bacterial count, with or without a swab test, for estimating cleanliness. Among these were from Langeveld et al. [1994]. However, Spenceley et al. [1994], found that such counts obtained on pipelines cleaned by circulation did not always correlate with film deposits, and concluded that bacterial counts could not be recommended as a sole measure of cleanliness. Such procedures, of course, reflect only the viable bacteria on the surface at the time of testing and give no index as to microbial growth potential or physical cleanliness of the surface.

Blanchard et al. [1998] has investigated biofilm disinfection from stainless steel surfaces using a formulation of peracetic acid and hydrogen peroxide. The work describes the influences of operating parameters on disinfection effectiveness under static and dynamic conditions.

1.7 TYPES OF CLEANERS

Harper [1972] specifies that to achieve a consistently acceptable cleaning procedure in a food operation, it is necessary to give consideration to the following:

1. Selection of an effective cleaning compound.
2. Determination of concentration needed to most economically accomplish the desired cleaning.
3. Selection of external energy factors to facilitate cleaning.
4. Method of application of the cleaning compound.

Cleaning compound selection depends upon a number of interrelated factors which include:

1. The type and amount of soil on the surface. The soil may be solid or liquid and will differ in shape and rheological properties
2. The nature of the surface to be cleaned.
3. The physical nature of the cleaning compound.
4. Method of cleaning available.
5. Quality of water available.
6. Cost.

1.7.1 Definition of a Detergent

A number of definitions have been offered for a detergent (Bourne and Jennings, [1963]). They have defined the term as "*A detergent is any substance that either alone or in a mixture reduces the work requirement of a cleaning process*". Detergency is a colloidal phenomenon; an effect that depends on the physicochemical behaviour of matter at phase interfaces. This definition includes soap, surface-active compounds, sodium hydroxide (not surface-active); polyphosphates that have synergistic effects and substances restricting the redeposition of removed soil (e.g. sodium carboxymethylcellulose). It also includes solvents and cleaners that function by chemical degradation (eg strong acids), since they reduce the work requirement to zero. However, it does not include abrasives since they do not reduce the work but only the efficiency of cleaning.

The work that needs to be supplied to remove the soil is of two types: namely mechanical and physicochemical energy. A detergent additive substitutes physicochemical energy for some of the mechanical energy required in removing the soil. A number of improvements have also been made to the remaining mechanical energy which has to be supplied for industrial cleaning processes.

Cleaning of a solid object (referred to as the substrate) involves the removal of unwanted foreign matter (soil) from its surface. The more restricted term "detergency" will refer to the cleaning effect obtained in a system having the following characteristics:

1. The cleaning is accomplished by a liquid medium, the bath.
2. The cleaning action of the bath is not due primarily to a dissolving action on the soil, although such dissolving action may take place on certain of the soil constituents. Nor is the cleaning action effected simply by hydraulic shearing of the bath against the soil substrate.
3. The cleaning effect is primarily caused by interfacial forces acting among substrate, soil and bath. These forces operate to loosen the soil-substrate bond and thereby facilitate soil removal.

When immersed in a bath, the system becomes a typical lyophobic colloidal system. The removal involves dispersing agglomerated mixed colloidal consisting of the substrate surface and the particles adherent to it.

Asher [1975] assessed the problems associated with commercial washing using detergents. He proposed that a detergent should possess some or all the following actions:

- **Wetting** or establishment of intimate contact between the surface and the cleaning agent.
- **Deflocculation** or the holding in suspension of removed soil down to micro-particle size and preventing these particles from clumping or coagulating.
- **Emulsification.** Caustic alkalinity is essential since it gives buffer action to the solution and is also responsible for the sterilising effect of an alkaline salt type of detergent.
- **Hydrolysis** which is the break up of fats, fatty acids, glycerides and soaps into manageable globules and simpler compounds.

1.7.2 Energy Relations in Detergency

Kling and Lange [1960], working with textile cleaning, made observations and conclusions of interest in other cleaning problems. On theoretical grounds, they postulated that the potential energy of a soil particle as a function from a surface is the result the electrical repulsive energy and the van der Waals attractive energy. In a detergent-free system, the lowest energy state, which would be the natural condition, is the adsorbed particle. The removal of this particle requires the overcoming of an energy barrier. This barrier is of a form that permits adsorption of suspended particles (including readsorption of removed particles). An important function of the detergent is to interact with this suspended particle and reduce its energy level. This effectively creates an energy barrier that has to be overcome before redeposition can occur. The reactions involved are discussed by Harris [1961], which include solubilisation and electrical repulsion between similar adsorbed layers. Jennings [1963] has determined values for the energy of activation E* for the reaction:

$$\begin{array}{c}\text{SOIL}\\ \text{DEPOSITED}\end{array} \xrightarrow{E^*} \begin{array}{c}\text{SOIL}\\ \text{SUSPENDED}\end{array}$$

Values of E* of the order of 8-9 kJ/mol were found for sodium hydroxide and a non-ionic surfactant detergent removal of milk films by Jennings.

Tachibana et al. [1960] studied the removal of beef tallow from bleached cotton cloth in a controlled and automatic washing device using sodium dodecyl sulphate as the detergent. In plotting the soil removed versus detergent concentration, they found a maximum beyond which higher detergent concentrations removed less soil. This result

result agrees with that of Bird [1993] in his study of whey protein cleaning from hard surfaces. However, the majority of detergency studies involving detergent concentration show that detergency increases to a limit and does not decrease again at high detergent concentrations (Plett [1985], Kane and Middlemiss [1985]). This is consistent with the theory that a detergent reduces the forces holding a thin film to a surface, but has no further influence above a concentration representing some kind of saturation effect.

Baier and Meyer [1985] have demonstrated the applicability of surface chemical principles to the rapid and effective displacement of contaminant films from solid surfaces. Surface-Active-Displacement Solutions (SADS) developed for cleaning residues from metal and plastic surfaces exhibited the additional beneficial features of corrosion inhibition, recontamination inhibition and low cost. Work is currently being done in this area.

1.7.3 Acids

Work involving the use of acids in the food industry are mainly based on the milk industry. Acids are used in combination with alkalis in a two stage cleaning process. Their principal function is in the dissolution of mineral based deposition or scale.

White and Rabe [1970], evaluated the use of nitric acid as a detergent in dairy CIP systems. They constructed a model CIP system and used an atomic absorption method to evaluate the detergency of low concentrations of nitric acid. Their results indicated that critical temperature-concentration combinations exist which remove calcium from stainless steel test plates soiled with a milk film. The stainless steel test plates that were soiled with milk became resistant to wetting with water after being washed with nitric acid.

1.7.4 Alkalis

The simple alkalis exert a strong cleaning effect on certain substrates because they furnish an excess of hydroxyl ions that charge and hydrate the surface.

The main actions of alkalis on a soil are saponification and dispersion, although they are also good surfactant enhancers and possess water softening characteristics. Their high pH aids in the destruction of many micro-organisms.

A great deal of work has been undertaken on the effectiveness of alkalis as cleaners, particularly sodium hydroxide for application in the Food Industry. Most of this work has involved the removal of tristearin and milk rather than application to starch soils.

The impact of alkaline commercial cleaning solutions are discussed by Graβhoff [1989]. The efficiency of these is discussed. The experimental fouling and cleaning work used 50 mm diameter plates, dried in air by varying both flow-rate and temperature.

1.7.5 Surfactants

Surface active agents (surfactants) are by definition, active at interfaces and energy is expended in aligning surfactant molecules at these interfaces. The changes that occur to a surfactant as a result of concentration or temperature effects, have a direct impact on adsorption and solubilisation and these imply a greater or lesser energy change (Vincent [1985]).

The key to surface activity lies in the highly asymmetric structure of the surfactant molecule. Molecules of the aqueous surfactants are typically elongated, having one side that is nonpolar and hydrophobic, the other end being polar and hydrophilic. The term "amphipathic" has been applied to this type of structure. The balance between the two ends with regards to both the mass and polarity is such that the compound is water-soluble, but the solutions have several unusual characteristic properties. One of the most notable is that the surfactant has a strong tendency to become adsorbed at most phase boundaries of the solution regardless of the chemical nature of the bordering phase. Adsorption at the air/water interface is responsible for the low surface tension. The molecules tend to be orientated in the adsorbed layer with the polar end towards the polar phase and the nonpolar end towards the nonpolar phase. There are thus relatively few phase interfaces involving aqueous solutions that will not have their free energy reduced by an adsorbed layer of surfactant.

A second unusual property of surfactants is that their molecules associate into soluble micelles when the solution reaches a certain critical concentration. The association is reversible. This critical concentration for micelle formation (the cmc), is characteristic for the surfactant species. For most surfactants that are used in detergent formulations it is in the range 10^{-4}-10^{-2} *M*. Above this concentration the aqueous surfactant solution is capable of dissolving considerable quantities of various organic materials that are quite insoluble in pure water. Solubilisation is attributed to molecular association of the material being solubilised with the hydrophobic portion of the surfactant. The extent to which solubilisation occurs is dependent not only on the chemical constituents of the surfactant and soil respectively, but also on the structure of the micelle (i.e. the number and arrangement of surfactant molecules composing it). In general, micellar structure changes in a discontinuous manner as the concentration is increased above the cmc. The micelles which form first are roughly spherical or equi-dimensional in shape, and may contain from 50 to 500 molecular units. These are arranged with the hydrophobic "tails" tucked together in the interior of the structure and the polar "heads" in the exterior adjacent to the aqueous solvent molecules. At concentrations roughly 10-50 times the cmc the micellar structure of many surfactants changes drastically. The molecules assume a long-range order and in some instances appear to form a liquid crystal structure. The cmc itself, the "secondary cmc" at which the micellar form changes and the detailed structure of the micelles themselves are affected by temperature, by the presence of salt and other non-surfactant solutes, and by the presence or absence of solubilisable organic material.

The electrical charge characteristics of surfactants have an important bearing on the detersive properties. Surfactants are classed as anionic, cationic, amylophytic (or amphoteric) and nonionic, depending on the charge of the ion which contains the hydrophobic group.

Cationic surfactants are seldom used as detergents since the majority of substrates are negatively charged and hence impractical high concentrations are required to prove effective.

Anionic surfactants behave in just the opposite manner. They adsorb onto positively charged surfaces by van der Waals and/ or hydrophobic bonding, orientating with their polar heads outward. They are relatively easy to desorb by rinsing. Amylophytic surfactants behave like anionic at high pH and like cationics at low pH. The pH acts in two ways: it affects the degree of dissociation of weakly ionised surfactants and it also affects the surface charge on the substrate, which comes into an adsorption equilibrium with H^+ and OH^- in the surrounding medium.

Nonionic surfactants are generally less firmly adsorbed than either of the ionogenic types. They tend to be sorbed via a van der Waals or hydrophobic bonding mechanism and orient with their hydrophilic groups in the aqueous phase. Most nonionics owe their solubility to a plurality of either oxygen and/ or hydroxyl groups (Espig [1997]).

Detergency studies were made on various types of washing products by Ruiz [1972]. He found that by washing raw milk films from glass surfaces by a devised mechanical apparatus and measuring the result in terms of light transmission using a spectrophotometer that an appreciable difference in detergency was found by the detergent material and variations in washing procedure. The highest detergency values were found with solutions prepared of near-neutral wetting agent and metaphosphate mixtures. The next in order of detergency were slightly alkaline wetting agent detergent, alkaline salts containing wetting agent, alkaline salts containing metaphosphate and acid detergent solution which gave lowest and entirely inadequate detergency.

1.7.6 Enzymes

Proteins and starches are present in significant quantities in food stains. The moderate water solubility of these polymers make them difficult to remove with classical techniques. Enzymes are highly specific catalysts that assist in the breaking down and removal of organic matter. The major types of enzymes are proteases which assist in the removal of proteins, lipases which assist in removing fats, and amylases which act on starches. The enzymes are not used up in this process. Such enzymes are currently used in laundry detergents and even in automatic dishwashing detergents. However, their use is not widespread in the food cleaning industry. This is due to several factors:

1. Instability at high pH level and over time. At present, enzymes can only be stabilised in the pH range of about 5-9 whereas an alkaline detergent has typically a pH around 12. An elegant way to proceed to stabilise the enzyme structure in built liquid laundry detergents is to use a borax-glycol complex to reduce the water activity.
2. There is a high cost associated with the purchase, stabilisation and formulation of effective detergents from the enzyme.
3. There is a concern that residual enzyme activity can affect the quality of the food products.
4. Enzymes are not compatible with available chlorine.
5. Enzymes act relatively slowly compared to conventional detergents and hence, enzyme cleaning requires longer times.

Both constituents of starch, namely amylose and amylopectin, are rapidly hydrolysed by α-amylase. This enzyme hydrolyses internal α-1,4 linkages to yield dextrins.

When any dispersed starch is fully hydrated it is completely hydrolysed *in vivo*. This type of material is found in mashed, freshly cooked starch foods. However, starch usually occurs in foods in complex solid structures whose features have an influence on the hydrolysis pattern. For instance, native starches form semi-crystalline structures which can be considered as an amorphous matrix in which more resistant regions are embedded. The fraction of total crystalline material is considered to be an important factor in defining the rate and extent of enzymatic hydrolysis (Planchot *et al.* [1997]).

In a mechanistic description, the amylolysis of solid substrate (Figure 1.3) involves three steps which limit the kinetics and extent of hydrolysis: diffusion of the enzyme molecule, adsorption of enzymes onto solid substrates and the catalytic event. The diffusion of enzyme molecules inside the substrate is determined by the porosity of the solid substrate and the diffusion coefficient of the enzyme inside the pores.

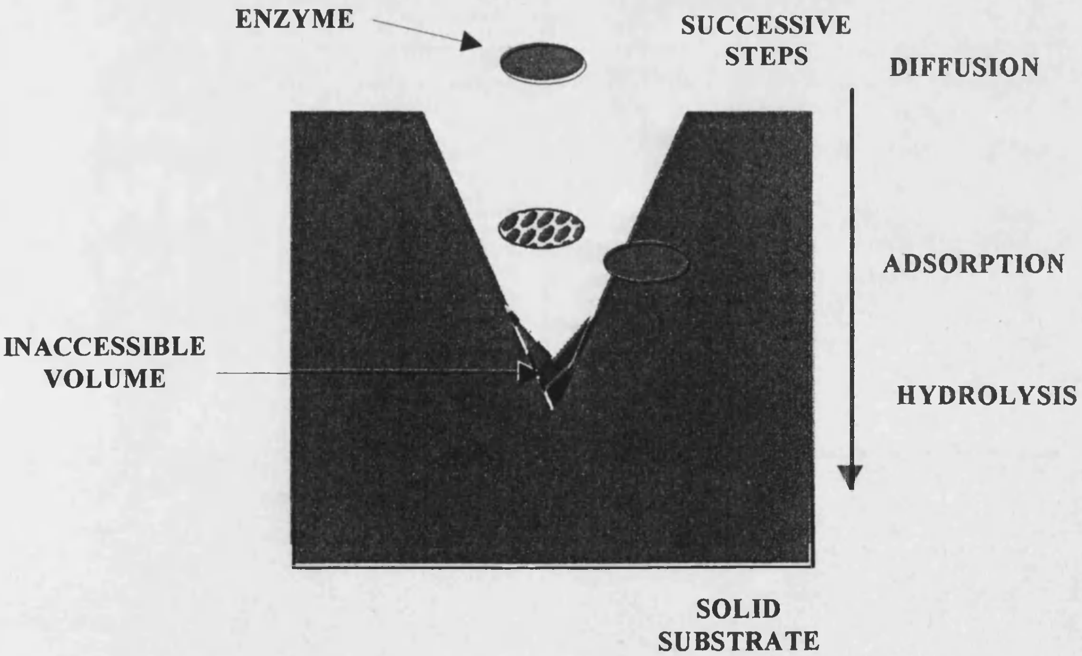


Figure 1.3 Three successive steps in enzymatic hydrolysis of an insoluble material (after Planchot et al. [1997])

1.8 CONCLUSIONS

The literature highlights the fact that cleaning is a problem. The cleaning of food process plant and equipment is necessary to ensure hygienic operation and maintain product quality. The degree of cleaning is dependent on a number of inter-related factors. Cleaning procedures are of environmental concern as they generate large quantities of effluent containing potentially harmful chemicals. High costs are associated with the disposal of such effluents and with lost production due to the downtime needed for cleaning. Traditionally, in the food industry, cleaning chemicals have been selected on an empirical basis which has led to subsequent problems. Therefore, the elucidation of cleaning mechanisms and the subsequent design of efficient cleaning protocols is important for both economic and environmental reasons.

1.9 SCOPE & OBJECTIVES OF THIS STUDY

The knowledge obtained so far in the field of starch cleaning technology shows that the following deficiencies still exist:

1. Insufficient knowledge of the mechanisms involved during the starch cleaning process.
2. Insufficient studies on the modelling of the kinetics of starch removal from hard surfaces using chemical cleaning agents.
3. Lack of a test methodology for measuring starch removal directly and indirectly.

The following objectives for the current research study have been chosen to address some of these shortfalls:

1. Development of a protocol for the experimental determination of starch removal from stainless steel using chemical cleaners.
2. Determination of the influence of the operating parameters on the kinetics of the cleaning process.
3. Modelling of the mechanisms taking place during the cleaning process. This modelling may test the applicability of existing cleaning models, which were really developed for protein removal.
4. Optimisation of the operating parameters with respect to energy and detergent consumption as well as required cleaning time.
5. Isolate effective cleaning formulations to minimise the environmental impact of the starch cleaning process.

1.10 STRUCTURE OF THESIS

This thesis has been structured into 6 subsequent chapters which deal with these objectives:

Chapter 2: **Fouling.** A discussion into the role of starch in baked foods and the problems caused by baking is provided.

Chapter 3: **Cleaning Kinetics and Modelling.** The influence of operating parameters on cleaning kinetics and their implications on modelling are discussed.

Chapter 4: **Project Development.** A literature review of both direct and indirect measuring methods employed to measure soil removal is described. This is followed by a description of the fouling and cleaning protocols developed to determine starch deposit removal kinetics.

Chapter 5: **Experimental Results & Discussion.** A quantitative cleaning experimentation of static and dynamic starch deposit cleaning is described. A discussion of the effect of different parameters on the removal rate as well as the economic implications in industrial situations is provided.

Chapter 6: **Modelling Removal.** Models are developed from the experimental data obtained to describe the starch removal process in a dynamic system

Chapter 7: **Conclusions and Future Work.** Conclusions drawn from this project are summarised and areas for further investigation are discussed.

1.11 PUBLICATIONS ARISING FROM RESEARCH

The publications arising from this work were:

- **Din, RA**, and Bird, MR, 'A kinetic study of starch removal from hard surfaces using chemical cleaning agents' *Proceedings of Food Process Engineering*, The 4th Bath Food Engineering Conference, Bath, Avon, 19 - 21 September 1994.
- **Din, RA**, and Bird, MR, 'The kinetics of starch removal from hard surfaces using chemical cleaning agents' *The 1995 IChemE Event*, Edinburgh, 5 -6 January 1995, pp1157 - 1159.

- **Din, RA**, and Bird, MR, 'Removal of starch based deposits from stainless steel surfaces using chemical cleaning agents' *The Vth Symposium on Colloid and Surface Chemistry*, Timisoara, 25 - 27 September 1995, p1.

- **Din, RA**, and Bird, MR, 'The effect of water on removing starch deposits formed during baking' *The 1996 IChemE Event*, Leeds, 2-3 April,1996, pp187 - 189.

- **Din, RA**, and Bird, MR, 'A study of wheat starch deposit removal from stainless steel surfaces using chemical cleaning agents' *Starch: Structure and Function*, Edited by P.J. Frazier, P. Richmond and A.M. Donald, Published by The Royal Society of Chemistry, 1997, pp259-260

- **Din, RA**, and Bird, MR, 'Cleaning baked wheat deposits from hard surfaces' *Cereals: Novel Uses and Processes*, Edited by G.M. Campbell, C. Webb and S.L. McKee, Plenum Publishing, 1996, Chapter 13 pp103-106

- **Din, RA**, and Bird, MR, 'A kinetic study of the chemical cleaning of baked wheat starch from stainless steel surfaces' *Proceedings of Starch 96*, Netherlands Institute for Carbohydrate Research, Noordwijkerhout 7 - 8 October, 1996.

- **Din, RA**, and Bird, MR, 'The removal of baked wheat starch deposits from hard surfaces using aqueous chemical cleaning agents' (Refereed paper) orally presented at the *AIChE Conference*, Chicago, 10-15 November, 1996.

- **Din, RA**, and Bird, MR, 'Cleaning baked wheat starch deposits using enzymes' (Refereed paper) orally presented at the First European Symposium on *Enzymes in Grain Processing*, Leeuwenhorst Congress Centre, Noordwijkerhout 2 - 4 December, 1996. (Proceedings awaiting publication.)

- **Din, RA**, and Bird, MR, 'The removal of starch residues formed during baking by the use of aqueous chemical cleaning agents' (Refereed paper) *International Conference on Engineering and Food (ICEF)*, Brighton 13 - 17 April 1997, Part 2, H33-H36

* 1 further refereed paper awaits publication

* 1 article published in the IChemE Food & Drink Newsletter

Chapter 2: The Fouling Problem

2.1 INTRODUCTION

A prerequisite to any cleaning study is to understand the processes involved in fouling. An understanding of the processes which produce fouling and lead to cleaning must be coupled with a description in engineering terms in order for exploitation by process designers. This chapter aims to identify the fouling categories, mechanisms and their role in the food industry as related to starch. An experimental description of fouling reproducibility is given in Chapter 4.

The term fouling refers to the undesirable formation of inorganic and/or organic deposits on surfaces (Bott [1990]). The majority of the literature has been focused on fouling films in heat exchanger equipment. These films can impede the flow of heat across the surface, increase the fluid frictional resistance at the surface (Deplace *et al.* [1994]) and increase the rate of corrosion at the surface. In any case, energy losses result due to a decrease in the overall heat transfer coefficient, an increase in the pressure drop across the system due to an increase in surface roughness and decrease in flow cross-sectional area. Thus, the amount of heat transferred to the heat exchanger will decrease as a function of time.

Industrially, the fouling problem is a costly one: tentative estimates published by Bott [1990] suggest the annual cost of fouling related problems for a large chemical company was in the order of £5m per annum. This figure takes into account:

1. <u>Energy losses in using inefficient equipment</u>: Fryer [1986], showed that it was theoretically possible to predict an optimum combination of heat exchanger size and tube side temperature which would minimise the degree of fouling in a system. This model assumed that a single fouling reaction occurred in the region of the wall at the wall temperature.
2. <u>Maintenance and cleaning costs</u>: Contamination of bulk product by fouled material and reduction in plant capacity has severe cost implications. The Food Industry responds in reducing these costs by the incorporation of foulant resistant heat exchangers; for example the surface scraped surface heat exchanger

(Margetti [1985]), which continually sweeps the transfer surface with rotating blades. However, incorporation of such devices results in an increase in initial capital expenditure. This expenditure has to be weighed up against the product safety risk if the heat treatment process is compromised.

However, the fouling problem is much broader than that related to heat exchangers alone and situations arise in the food industry which may be related to both heat and non-heat induced fouling (Hasting [1994]).

2.2 TYPES OF FOULING

Several types of fouling and their combinations may occur:

1. *Crystalline* or *Precipitation fouling*: due to the deposition or the formation of crystals from the solution on the surface.
2. *Particulate fouling:* accumulation of solid particles from the fluid stream onto the surface.
3. *Corrosion fouling*: effects of corrosion on the heat transfer surface.
4. *Chemical reaction fouling*: where the deposit is the result of one or more chemical reactions between the reactants contained in the flowing fluid.
5. *Biological fouling* or *bio-fouling*: the deposition and growth of organisms originating in the process stream on the surface (Blanchard et al. [1998]).

Examples of these types of fouling are given in Table 2.1.

HEAT-INDUCED FOULING	NON-HEAT INDUCED FOULING
Starch deposition in heat exchangers	Biofilm growth on process surfaces
Ice-cream deposits in chillers	Material accumulation in low flow areas of process equipment
Lime-scale up in cooling water systems	Membrane fouling
Biscuit burn-on in ovens	

Table 2.1 Examples of heat and non-heat induced fouling.

2.3 FACTORS AFFECTING FOULING

Many operational factors affecting heat-induced fouling have been identified either by observation of commercial equipment or experimental determination. The most widely recognised factors are:

1. Flow-rate of the heated material.
2. Temperatures of the surface on which foulant forms.
3. Bulk fluid temperature.
4. Type and nature of the surface on which the foulant forms.

Biofouling studies have been limited (Spenceley et al. [1998]). Investigations have most frequently been applied to fouling of heat exchangers by milk (Fryer [1986], Deplace [1997]) and coffee drinks (Takahashi et al. [1997]). In these studies, attempts were made to develop equations to predict fouling rates.

A great number of authors have studied fouling from milk-based fluids in a variety of heat exchanger geometries. Most of these authors have been cited by Belmar Beiny *et al.* [1993]. An important result of these investigations was the key role played by whey proteins, especially β-lactoglobulin, in the fouling process (Fryer et al. [1988], Zwietering and Hasting [1997]), it is well established that heat treatment causes unfolding of β-lactoglobulin . Such unfolding (often described using the general expression "heat denaturation") makes adhesion possible on heat transfer surfaces and then fouling of the heat exchanger.

According to Sandu *et al.* [1985], fouling dynamics are deduced by the thickness of the fouled layer on a heat transfer surface as a function of position and time for a given set of design process parameters, and finally yields a dependence of the fouling resistance and pressure drop in the heat exchanger subject to fouling. A discussion of the methods for monitoring fouling is given in the next section. Two widely employed methods are: for the measurement of fouling resistance -deduced from overall heat transfer coefficient determination; and the measurement of mean thickness of the deposit, deduced from the overall pressure drop. These methods are an adaptation of classical methods used in chemical engineering (Coulson and Richardson [1993]).

They lead to the following expressions:

$$R_f = \frac{1}{U} - \frac{1}{U_0} \tag{2.1}$$

where: R_f = fouling resistance and U and U_0 are the overall heat transfer coefficients in the presence and absence of fouling respectively. The fouling resistance can be expressed in terms of the deposit density and the deposit thermal conductivity:

$$R_f = \frac{\delta}{\lambda} = \frac{M_d}{\rho \lambda A_d} \tag{2.2}$$

where: δ =deposit thickness, λ= thermal conductivity, M_d = mass deposit, ρ = deposit density and A_d = deposit area.

The problem with applying this technique is the practical difficulty in measuring the thermal conductivity due to the non-uniformity of the deposit.

2.4 MONITORING FOULING

A number of methods have been developed to monitor fouling in industry:

1. Removable test sections of the fouled surface: This method is intrusive to the process and usually there is no means of testing how the deposit affects the system.
2. Pressure drop: This method has its limitations since a critical thickness or roughness of deposit has to be achieved before measurement is possible and is only applicable to pipeline and channel systems.
3. Heat transfer resistance monitors: This method is more sensitive than measuring fluid frictional resistance. However, the measured overall heat transfer resistance is influenced by two types of heat transfer resistance (overall = convective + conductive) and therefore is very deposit dependant.
4. Ultrasound: This technique is most advanced in the detection of fouling in ultra high temperature and continuous processing plants (Withers [1993]). However some work has been done in its use in the detection of starch deposits in pipes. Ultrasound has the advantage of being able to penetrate stainless steel pipe walls and thus providing the possibility of an on-line, non-intrusive and non-invasive sensor. However, several drawbacks lie with the use of ultrasound: if the liquid

contains gas bubbles or particular matter, then the signal being passed through it will be scattered by absorption. Secondly, scatter of a irregular food film can attenuate the signal as well as reflections inside the pipe system can be masked by the large reflection of signal caused by pipewall to fouling interface. Hence, at present the measurement of food film thickness is difficult.

The next section aims to describe the role of starch in the baking and fouling processes and the interactions involved in the formation of a deposit.

2.5 ROLE OF STARCH IN BAKED FOODS

The functionality of starch as a wheat flour component in bread baking processes has been discussed by Lillford and Morrison [1997]. It is established that the integrity of wheat starch granules is essential for their optimal performance both in bread and cake systems (Tester [1997]). Consequently, mechanical, chemical or biochemical disruptions of the native granule organisation have adverse effects on bread forming properties of wheat starch. In practice, those changes may be effected mechanically by over-milling and therefore starch damage limits are frequently included in baker's flour specifications. The effect of excessive starch damage is further aggravated by abnormally high levels of cereal α-amylase derived either from added malt or as a result of preharvest sprouting of the parent wheat.

Georget and Smith [1997] have shown that wheat starch is superior in baking quality to rice, corn, waxy corn and potato starches. In addition there are wide differences in the baking quality of starches from different wheat varieties.

The surface characteristics of the starch granules affect starch-protein interactions. The results of scanning electron micrographs showing starch granule structure in a wheat flour are given in Chapter 4. These show patches on the granule surface, termed adhering matter (AM) by Kulp and Lorenz [1981]. The researchers postulated that the adhering matter may serve as a linkage between starch and other flour components (proteins and lipids).

Compositional studies of adhering matter revealed that it contains proteins (water soluble and gluten type), starch polymer fragments and pentosans consisting of xylose, arabinose and mannose. The proteins contained thiol groups at a level similar to that of flour. Noteworthy was the presence of enzymes. The majority of α-amylase present in the flour was concentrated in the adhering matter and remained associated with the granules throughout the dough-making process.

2.6 CHEMICAL CHANGES IN STARCH PRODUCED BY THERMAL PROCESSING

During the baking process moisture at the surface of the baked food evaporates rapidly. Although water from the moist interior of the piece will diffuse to the surface and replace the water that has been evaporated, the rate of evaporation is relatively fast compared to the rate of diffusion. Therefore, as baking proceeds there is a gradient of decreasing moisture from the centre to the outside of the piece and the crust becomes very dry. It is the dry and hot surface which induces browning to occur late in the baking cycle.

The browning of most baked products is by Maillard-type reactions (Hoseney [1984] and Ames [1990]). The first step of these reactions is the condensation of the free amino group, usually from an amino acid, with the carbonyl of a reducing sugar. Since water is eliminated in the reaction, the reaction is favoured by dehydration conditions. After the condensation there are a number of rearrangements that lead to the brown pigmentation. Caramelization also takes place and is a complex series of reactions of sugars effected by heat. Both reactions proceed faster at high pH than at low pH.

Resistant starch (RS) is also a consequence of baking process resulting in caramelization and Maillard reactions (Rabe and Sievert [1992], Leloup *et al.* [1992]).

2.6.1 Polymer Properties Of Starch Under Thermal Processing

The melting and glass transition behaviour of starch strongly influence the processing and material properties. Endothermic energy is required to disrupt the crystalline areas of starch until melting occurs at a temperature T_m. On cooling, if crystallisation does not intervene, an amorphous liquid-like to solid-like transition occurs known as the glass transition temperature, T_g. Adding water to the crystalline or amorphous liquid results in the depression of T_m or T_g - the extent of which increases with the mass fraction of diluent and with increasing favourable interactions between diluent and the starch polymer. Figure 2.1 summarises the data that are currently available for the effect of water on the T_g and T_m of starch (Ring [1995]). The melting data relate to the A and B crystalline polymorphs of a short linear chain, and the glass transition data to a high molecular weight amylopectin (amylose behaves similarly). The picture shows that the A polymorph is thermally more stable, and that water has a strong effect on T_g.

Glass polymer solids such as those found in crisps and biscuits are very rigid and brittle, and even small deformations result in fracture. Above T_g however, the polymers become more rubbery - and even large deformations will be recoverable.

2.6.2 Starch Granule Modification According To Hydrothermic Food Processing

Native starch in the granule form is insoluble in cold water. When observed under polarised light, an aqueous suspension of starch gives rise to a characteristic polarisation cross, proving its microcrystalline structure (Rothwell and Garner [1986]). The structure is maintained by hydrogen bonds between the starch chains. Under dry heat conditions, starch granules are not disrupted and the polarisation cross remains unchanged (Bornet [1993]). In the cereal biscuit, a significant amount of the starch is not gelatinized in the crust because of the dry heat at the surface of the biscuit during cooking (Figure 2.2).

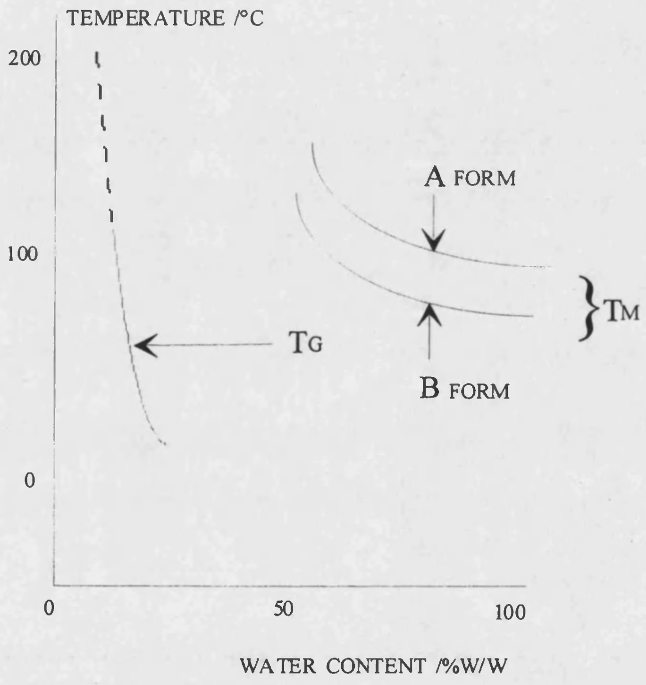


Figure 2.1: The effect of water as a diluent on the T_m of the short chains of amylopectin, and the T_g of the polymer (after Ring [1995]).

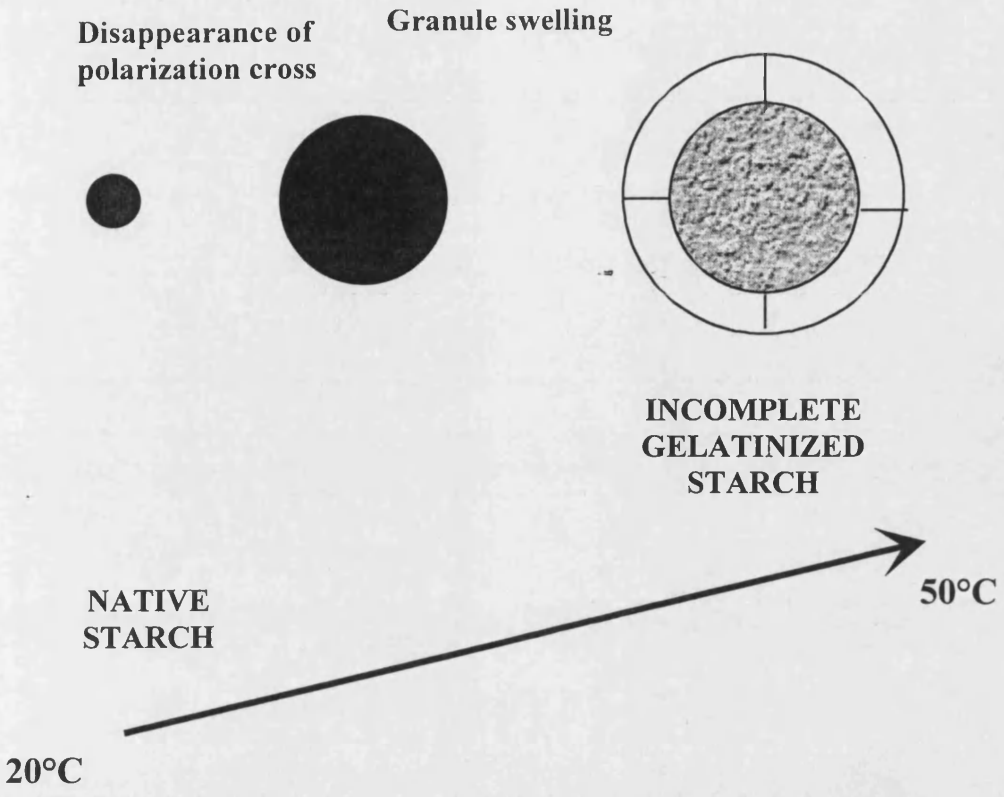


Figure 2.2: Native starch or partial gelatinized starch; caused by no heating or dry heating; typical in the crust of biscuit (after Bornet [1993]).

However, when sufficient water is present during heating, dramatic changes occur to the structure of the starch granule (Jane [1997]). The first change is the loss of the polarised cross. As the temperature increases, hydrogen bonds are disrupted and water is absorbed by the starch granules. This swelling is followed by a step of amylose leaching. The starch is progressively solubilised, gradually increasing the solution viscosity. This state of utmost disorganisation is a function of the gelatinization temperature, which varies according to the starch origin (Guilbot and Mercer [1985]) from 65 to 85^{o}C. At the same time, starch α-amylase susceptibility increases dramatically. A pictorial representation of the physical starch characteristic changes is given in Figures 2.3 and 2.4.

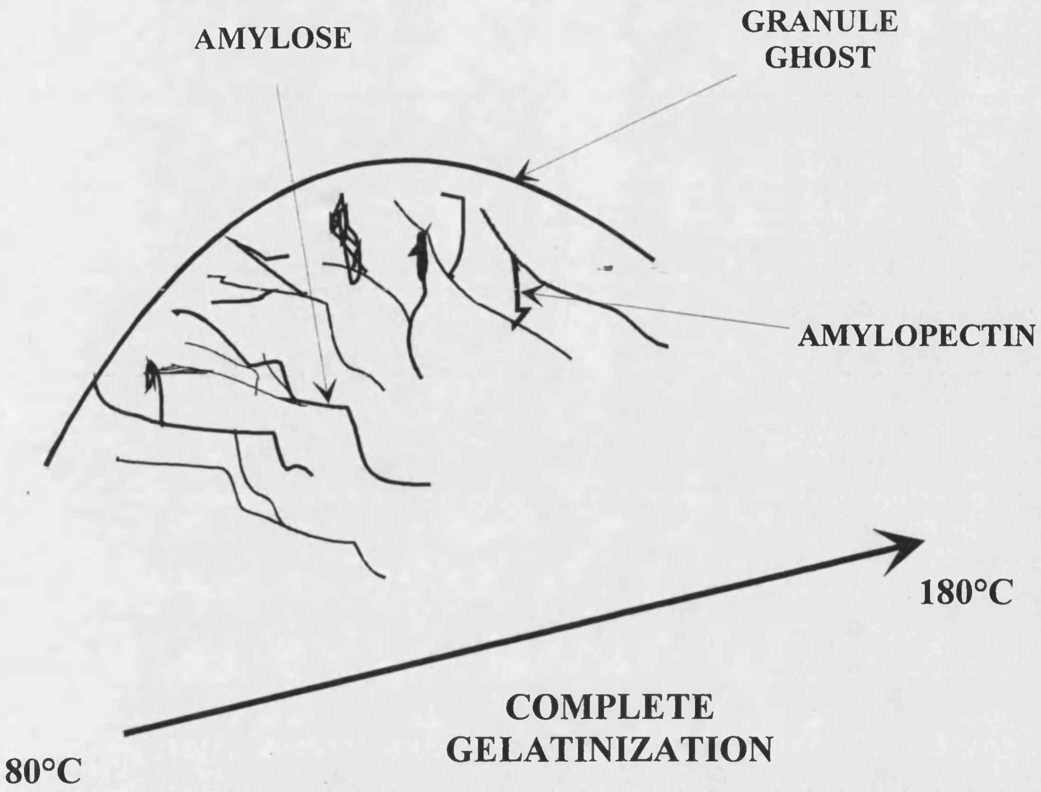


Figure 2.3: Gelatinized starch structure with disrupted structure found as a result of baking, drum-drying and extrusion cooking typical for flour cereals, bread baking and instant flour cereals. High moisture content results in disrupted starch structure with a high solubility.

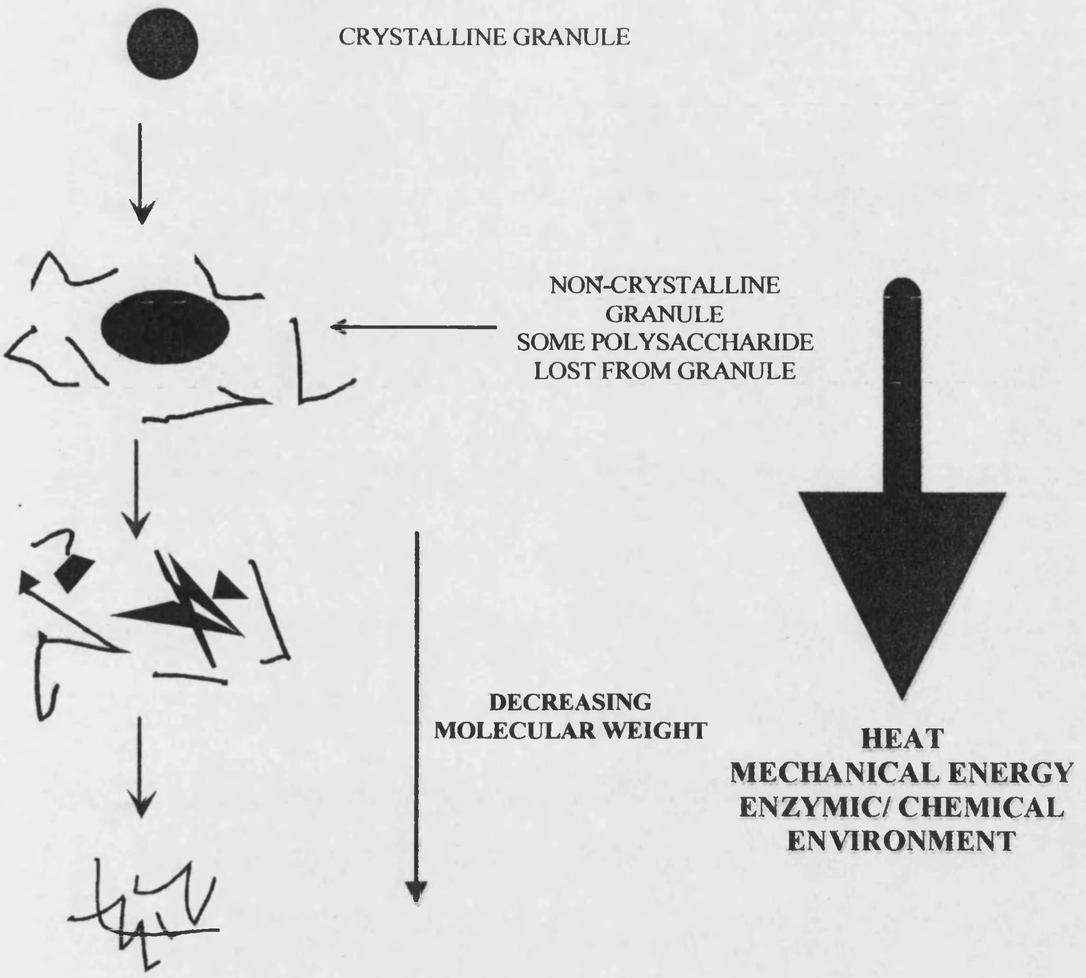


Figure 2.4: The behaviour of starch with increasing levels of conversion in excess water.

2.7 CHEMICAL BONDS IN DOUGH

Most cereal products require mixing flour with water to form a dough. Dough is a highly complex chemical system consisting of a number of constituents discussed in Section 2.5. According to Pomeranz [1988], food containing flour as the main constituent can be best differentiated from one another on the ratio of flour to water used in the manufacture. In dough systems, the ratio of flour to water is about 1:0.6, and the gluten proteins provide the main structural matrix. In systems of higher ratios of water to flour, the importance of the gluten matrix decreases.

To relate chemical composition to functional properties and explain chemical and physical modifications in dough processing, it is essential to understand the nature of the chemical bonds among dough components.

2.7.1 Types of Chemical Bonds in Proteins

Chemical bonds in proteins can be divided into two major types: covalent and noncovalent. The covalent bonds include bonds within the amino acid, bonds between the amino acids (peptide linkages) and disulphide (SS) links within or between peptide chains. The energy associated with (or required to break) those bonds is high. In addition, noncovalent bonds include ionic, hydrogen and van der Waals bonds, which are generally much weaker than covalent bonds.

In addition to the chemical bonds, there is the hydrophobic bond. Hydrophobic and van der Waals bonds have one thing in common: both are significant in interactions between nonpolar groups. However, the hydrophobic bond is not a chemical bond (i.e. due to the attraction between protons and electrons) but a thermodynamic phenomenon or entropy effect favoured by increasing the temperature up to about 60°C. They could be a contributory factor to the elasticity displayed by a dough.

Some of the amino acids in gliadin and glutenin are charged (Pomeranz [1988]). Theoretically, these ions may improve both the association and dissociation of dough components. However, no literature has been found to support this hypothesis.

The hydrogen bonds result from the affinity of hydrogens of hydroxyl, amide, or carboxyl groups for the oxygen of carbonyl or carboxyl groups. These bonds play a significant role in the cohesive properties of gluten. However, the most effective hydrogen-bond-forming components in wheat flour, in addition to water, are pentosans. The total (soluble and insoluble) pentosan content of flour is only about 1.5%, but pentosans can absorb 15 times their own weight of water (Tester [1997]). Therefore, up to 13% of the water in dough could be bound to pentosans. Although most hydroxyl groups of the flour are in the starch, the starch granules are so tightly packed that only groups at the surface are available for hydrogen bonding. The specific surface of starch is 0.1249 m^2/g (Gracza and Greenberg [1963]). In 100 g of dough there is about 44 g of starch, which absorbs 8.7 g of water, corresponding to about 3.5 monomolecular layers of water around the starch granules. During baking, the starch granules swell and gelatinise and absorb most of the water. The role of glutamine, the major amino acid and a strong hydrogen-bond-forming residue of wheat proteins is well established. Naturally present sugars further increase the content of polar substances that may participate in hydrogen bonding.

2.8 CONCLUSIONS

Fouling is a complex process involving a number of interrelated factors and is apparent in the food industry in a number of different ways. It results in heat transfer, frictional flow resistance and microbial contamination problems in the process plant.

A number of food fouling studies have focused on milk and its products due to the significant heat-induced fouling produced. However, little work has been conducted to investigate starch fouling although this is a major problem in the food industry.

Starch plays an important functional role in baked foods and the surface characteristics of starch granules affect interactions between other flour components. The melting and glass transition behaviour of starch strongly influences the processing and material properties. A number of dramatic changes occur to the native starch granule as a result of hydrothermic processing and this change is very dependent on the degree of gelatinisation. The browning of most baked products is by Maillard and caramelisation reactions and result in the formation of a resistant starch (RS). The main forces responsible for the bonding in wheat flour are hydrogen bonding and van der Waals forces.

Although fouling can be reduced in food processing it is unlikely to be eliminated and a fundamental knowledge of cleaning process is necessary (Chapter 1). A prerequisite to the design of an effective cleaning strategy is a knowledge of the fouling mechanisms in the starch substrate being studied and the deposit formed as a result of hydrothermic processing.

CHAPTER 3: CLEANING KINETICS AND MODELLING

3.1 INTRODUCTION

The study of cleaning dynamics allows a prediction of the time and operation conditions necessary to achieve any desired level of cleanliness. It is therefore necessary to develop a mathematical model. Modelling also enables us to predict the outcome of cleaning outside the range of normal operation when experiments are difficult or expensive to perform. It also tests the validity of the mechanistic assumptions with the experimental results obtained.

3.2 REVIEW OF CLEANING MODELS

Most of the classic cleaning modelling was carried out during the 60's and 70's: the most representative studies are those carried out by Jennings [1957, 1959ab, 1960, 1961, 1963ab, 1965]; Bourne and Jennings [1961, 1963abc] and Schlussler [1970,1976]. When cleaning complex heterogeneous protein rich soils, these authors chose an empirical modelling of the phenomena because they wanted to show a practical application, but also because of the complex mechanism involved (Jennings et al. [1957]; Jennings [1959ab, 1960]; Schlussler [1970]). In order to know the role of the mechanisms during cleaning, they subsequently worked on homogeneous soils of a simpler composition; tristearin deposit in the case of Bourne and Jennings [1961, 1963abc] and triolein deposit for Schlussler [1976]. However, their results based on an analogy with chemical reaction theory for these model soils are extremely limited and cannot in any case be applied to the cleaning of heterogeneous soils such as starch.

Maruyama et al. [1991], have developed a practical method of determining cleaning rate for starch deposits. They have considered the use of mass transfer theory to predict cleaning rates, effect of dead space in systems as well as the exfoliation on the rate of mass transfer in piping. They found that the removal of starch progressed at a constant rate. This showed that the controlling factor was solubility of the solute and exfoliation was not a factor.

Schlussler [1970] cleaned milk, butter milk and chocolate milk samples deposited on glass strips of 30 cm^2 and dried them at low temperature (maximum 40°C). The strips were immersed in a stirred vessel containing sodium hydroxide solution. The assessment method was based on a visual observation of the surface wettability by water. This gave a very inaccurate answer (negative or positive) which cannot be considered as satisfactory. Nevertheless, Schlussler experimentally determined the cleaning time necessary to eliminate the soil, whose initial quantity was determined beforehand. Then, he chose an average cleaning rate supposed to remain constant. This process cannot give any cleaning aspect versus time and, being considered zero order reaction, a true kinetic study of the phenomena cannot be done. Average cleaning rates were obtained (between 0.16 and 1.3 g/s m^2) which led to cleaning durations between 30 and 150 s. On this basis, Schlussler studied the influence of a certain number of parameters on the cleaning process rate (temperature, nature and concentration of detergents, mechanical action, kind of soil, surface state). He proposed an empirical model relating the cleaning time to the temperature and the detergent concentration.

Schlussler [1976] defined the mechanism proposed by Harper [1972] more precisely by assuming that only the transport of cleaning solution to the soiled surface and the dispersion of the soil in the deterging medium influenced the speed of the cleaning process. He also proposed that these steps were characterised by diffusion processes taking place in the boundary between the soil deposit and the cleaning solution passing over it. Schlussler also proposed that the dispersion of soil into the deterging medium determined the speed of the cleaning process, since the hydroxide ions diffuse more rapidly through the boundary layer to the soil deposit than the reaction products diffuse into the cleaning solution. This is due to the size of the reaction products and their electrical charge. For this stage, Schlussler set up the first mechanistic approach, which is based on Fick's First Law. He showed that the cleaning rate constant k_r, defined for modelling the cleaning process, is as significant as the cleaning rate constant k defined by Jennings, who regards the cleaning process as a first order reaction. Schlussler also attempted to model the cleaning process by a simple first order reaction model despite its complexity.

Jennings et al. [1957] and Jennings [1959ab, 1960] steamed to dryness a few millilitres of ^{32}P labelled milk for use in cleaning experiments. The deposits were placed on 4.5 cm^2 stainless steel disks. The disks were inserted into a cylindrical pipe parallel to the circulation flow of the cleaning solution. Using radioactive counting, these authors obtained cleaning aspects versus time by taking one disk after another. Their conclusion was that the elimination rate of the deposit (*dm/dt*) was proportional to the quantity of deposit (*m*) present on the surface at each moment and to the concentration of the hydroxide ion (C_{OH}). They proposed the following relation:

$$-\frac{dm}{dt} = k' \cdot m \cdot C_{OH} \tag{3.1}$$

However, the model could only be applied to the elimination of about 60% of the initial deposit. In fact, the authors considered that at the end of the elimination process specific linkage phenomena with the surface occurred and that the subsequent kinetics was no longer represented by equation (3.1). The influence of the sodium hydroxide concentration was studied on a restricted range (0 to 0.6 wt%).

It is therefore impossible to apply equation (3.1) more generally. For this reason equation (3.2), which corresponds to a first order reaction in deposit mass is more commonly used as a basic cleaning equation (Paulsson and Tragardh [1985]):

$$-\frac{dm}{dt} = k \cdot m \tag{3.2}$$

Jennings [1959b] studied the influence of the temperature, sodium hydroxide concentration and mechanical effect on the cleaning rate constant (*k*) which ranged between 0.01 and 0.2 s^{-1}.

A review of kinetic models is presented by Plett [1985] and summarised in Table 3.1. The simplest models consider the transformation of the attached soil *S* to a final compound *F* which is dissolved, suspended, or emulsified in the detergent solution. Depending on the model chosen, the rate constant has different units and there has been no uniformity in expressing the soil amount S, as concentration per unit of surface or as total amount. This is significant if the model used is not first order reaction.

Reaction order	**Model**	**Author(s)**
zero	$-\frac{\Delta S}{\Delta t} = k_0$	*Schlussler [1970]*
first	$-\frac{dS}{dt} = k_1 S$	*Jennings [1965]* *Schlussler [1976]*
first / parallel	$-\frac{dS}{dt} = k_1 S_1 + k_{12} S_2$	*Bourne & Jennings [1963]*
first / sequential	$-\frac{d \ln F}{dt} = k_{1i}$ i = 1,2 = f(t) i = 1,2,3 = f(t)	*Thor & Loncin [1978]* *Plett & Loncin [1981]*

Reaction Scheme: $S \rightarrow F$ or $S_1 \rightarrow F$, $S_2 \rightarrow F$

Table 3.1 Kinetic Models Used in Cleaning (after Plett [1985]).

Gallot-Lavallee and Lalande [1984], developed a mathematical model for turbulent flow cleaning processes from hard surfaces based on physico-chemical mechanisms. The model accounts for different successive phases and is described by two first-order reactions taking place consecutively:

1) Diffusion of detergent through external boundary layer.
2) Diffusion of detergent into the soil.
3) Reaction between soil and detergent.
4) Back-diffusion of solubilised soil through external boundary layer.

The model assumes that, due to reaction with the hydroxide ions, the deposit changes from an original state S to an intermediate state I before it is removed and can be traced in the cleaning solution in its final state F, as depicted in Figure 3.1.

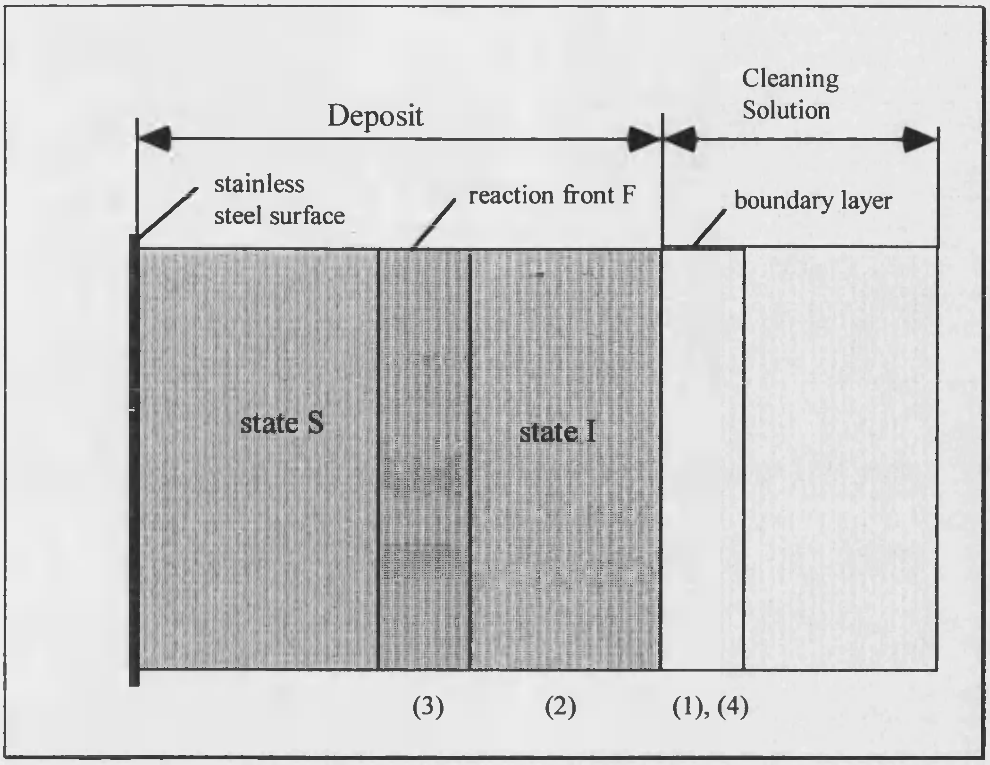


Figure 3.1 Schematic diagram of the cleaning process modelled by Gallot-Lavallee & Lalande [1985].

A modified numerical model of Gallot-Lavallee is presented by Bird [1993] who proposed that a whey protein deposit consists of two layers: a swollen and unswollen layer. Both these layers exhibit different removal patterns and two rate constants (k_o and k_1) are proposed. The results of his modelling showed that both the swelling parameter (k_o) and the deposit removal parameter (k_1), appear as functions of cleaning solution temperature, velocity and concentration. They can be represented by Arrhenius type expressions.

This type of model also takes into account the formation of the intermediate deposit state *I*, which is also described by Sandu [1981], Plett [1985], Graβhoff [1983] and Bird and Fryer [1991] before the soil reaches its final state *F*. The model set up by Gallot-Lavallee et al. [1985] is given in Table 3.2. It presumes that the cleaning rate at time t = 0 is zero, which is an experimentally verifiable observation. In their experiments they used an optical sensor to detect the soil in its final state *F*, which is carried away in the cleaning solution. Their study has shown that the results of the experiments can be depicted as a kinetic model with two identical reaction constants without affecting the accuracy.

Reaction Order	**Model**	**Author(s)**
First	$\frac{dF}{dt} = \frac{k_{11} \cdot k_{12}}{k_{11} - k_{12}} S_0 \cdot (\exp^{-k_{12} \cdot t} - \exp^{-k_{11} \cdot t})$	*Gallot-Lavallee [1985]*
First	*special case*: $k_{11} = k_{12} = k_1$ $\frac{dF}{dt} = k_1^2 \cdot S_0 \cdot t \cdot \exp^{-k_1 t}$	*Gallot-Lavallee [1985]*

Reaction scheme: $S \rightarrow I \rightarrow F$

Table 3.2 Models for cleaning kinetics based on reactions in series.

The presence of an intermediate compound *I*, which will cause an "induction period" in the formation of the final deposit state *F*, has also been used by Graßhoff [1983] to explain the initial increase in pressure drop when cleaning a piece of fouled equipment. This is due to the significant swelling of the fouled layer when contacting the detergent solution. Once this swollen layer (intermediate product *I*) is formed it will react further and the product *F* will be transported into the detergent solution.

3.3 INFLUENCE OF OPERATING PARAMETERS ON CLEANING KINETICS

According to Jennings [1965], the formation of a soil is regarded as a spontaneous process which is energetically favourable. Energy must therefore be supplied to reverse this natural state of a fouled surface. This is supplied in the form of chemical, thermal or mechanical energy during cleaning. Consequently, the parameters influencing the cleaning process are detergent concentration, temperature and the mechanical influence expected by the flow of the cleaning solution. The cleaning time is considered to be a dependent variable and is a function of the choice of the operating parameters and not an independent variable to be specified in cleaning experiments.

3.3.1 Influence of detergent type and concentration

The chemical composition of the detergent selected depends primarily upon the type of soil to be removed. This has been discussed in detail in Chapter 1 Section 1.7.

The detergent concentration (particularly with reference to alkalis), has been the subject of numerous studies. Table 3.3 summarises the results of cleaning experiments by various workers.

Model	**Concentration C_{OH^-} in %**	**Author**
$k_1 = a \cdot C_{OH^-}$	<0.6	*Jennings [1959, 1963, 1965]*
k_0 (non-linear)	0.2-3.0	*Schlussler [1970]*
$\ln k_1 = a + b \cdot C_{OH^-}$	0.1-3.9	*Gallot-Lavallee [1985]*

Table 3.3 Models for the influence of detergent (OH^-) concentration on the cleaning rates.

Jennings [1959, 1963, 1965] found a direct proportionality between the cleaning rate constant k and the sodium hydroxide concentration. The results apply for the concentration range up to 0.6%.

Schlussler [1970], found a non-linear dependence between the mean cleaning velocity $\overline{R_v}$ and the detergent concentration between 0.25 and 3 wt%. The optimum concentration range was between 1-3 wt%. An increase in concentration caused a decrease in overall cleaning rate. Schlussler put this phenomenon down to an adverse inhibition of the transport mechanism of the reaction products in the soil matrix.

A confirmation of this inhibition behaviour of high cleaning concentrations was observed by Bird [1993]. Although he did not propose a mathematical model for cleaning concentration, he determined the existence of a distinct optimum concentration for cleaning whey protein deposits with sodium hydroxide (0.5 wt%). A mechanistic model was developed which proposed that the optimum hydroxide concentration leads to a deposit with the highest voidage whilst higher or lower concentrations lead to a deposit with a lower voidage, and hence more resistance to removal by fluid mechanical shear.

3.3.2 Influence of detergent temperature

Increasing the detergent solution temperature generally enhances cleaning rate up to a point. The existence of temperature optima for microfiltration membranes fouled with whey protein has been demonstrated by Bird and Bartlett [1995]. Temperature effects on cleaning rates for homogeneous processes use the Arrhenius type equation for modelling. This has been used in models by Jennings [1959], Schlussler [1970] and Hoffmann & Reuter [1984]. However, the presence of an optimum cleaning temperature beyond which the cleaning rates decline due to the heat alterations of some soils implies that the simple Arrhenius model is not valid over the whole range of applicable cleaning temperatures. Gallot-Lavallee and Bird identified this problem and developed exponential models to describe the phenomenon. Since the rate of removal of soil (*dm/dt*) as proposed by Arrhenius is given by:

$$\frac{dm}{dt} = A \exp - \left(\frac{E}{RT}\right) \tag{3.3}$$

A = Exponential Constant

E = Activation Energy

For diffusion controlled processes E < 20 kJ/mol and for reaction controlled processes E ~150-300 kJ/mol. Experimentally determined values of activation energies were ~80 kJ/mol, indicating that cleaning is neither reaction or diffusion controlled but a combination of both.

A summary of the review of literature is found in Table 3.4.

Model **(T = t_R+273 in K)**	**Temperature** **t_R in ^oC**	**Author**
$\ln k_1 = a - \frac{b}{T}$	46-82	*Jennings [1959]*
$\ln k_0 = a - \frac{b}{T} \quad T < T_{max}$	5-100	*Schlussler [1970]*
$\ln k_1 = a - \frac{b}{T}$	40-80	*Hoffmann [1984]*
$\ln k_1 = a + b \cdot T$	55-95	*Gallot-Lavallee [1985]*
$\ln k_1 = a + b \cdot T$ $\ln k_o = a + b \cdot T$	25-73	*Bird [1993]*

a, b are positive constants

Table 3.4 Models for the effect of temperature on the cleaning rate constant.

3.3.2 Influence of mechanical action

Mechanical energy can be modelled by using the Reynolds number (*Re*), the wall shear stress (τ), or the mean flow velocity (v). Jennings [1957], Hankinson & Carver [1968] and Schlussler [1976] all proposed a minimum Reynolds number of 25,000 for mechanical effect to be significant. Cleaver and Yates [1973] stated that turbulent flow is required before removal occurs. However, other workers find steady removal at very low velocities in laminar flow (Bird [1993]).

Timperley [1981] and Graβhoff [1983], both agree that CIP in dairy pipes using sodium hydroxide is better correlated to the mean velocity and hence to the wall shear stress than to the Reynolds number. High shear stresses can be induced through turbulent flow conditions. Graβhoff reported a significant increase in the cleaning rate when the flow direction over the fouled layer is periodically inverted every 5 or 15 seconds. This suggests that the amplitude and frequency of "shear stress peaks" occurring in "turbulent bursts" have an important role in cleaning. The most extensive study was carried out by Paulsson [1989] who experimented on the mechanical effect of removal of clay deposits in turbulent pipe flow at Reynolds numbers between 8000-80000 under ambient conditions.

A summary of the models proposing the influence of mechanical effect are shown in Table 3.5.

Model	Range of validity for Reynolds Number. Re, Wall Shear Stress τ_W (in Pa) Mean Flow Velocity v (m/s)	**Author(s)**	**Foulant**	**Cleaner**
$k_1 = a + b \cdot \mathrm{Re}$	Re = 2500-35000	*Jennings [1957]*	Milk	NaOH
$\ln k_1 = a + b \cdot v$	v = 0.3-1.9	*Gallot-Lavallee [1982]*	Milk	NaOH
$k_1 = a + b \cdot \tau_w$	τ_W = 1-14	*Timperley [1981]*	Milk	NaOH
$\ln S = a - b \cdot \tau_w$	τ_W = 1-49	*Hoffmann & Reuter [1984]*	Milk	
$\ln S = a - b \cdot \ln \tau_w$	τ_W = 0.19-7.5	Graβhoff *[1983]*	Milk	NaOH
$k_1 = a + b \cdot \tau_w^{1.24}$	τ_W = 0.05-2.0	*Paulsson [1989]*	Clay	Water
$k_1 = a + b \cdot \mathrm{Re}$	Re = 350-7500	*Bird [1993]*	Whey Protein	NaOH

a, b are positive constants

Table 3.5 Models for the hydrodynamic effect on the cleaning rate constant.

3.4 CONCLUSIONS

The study of the literature has shown that the complexity of the cleaning process presents a difficult modelling problem. However, by studying cleaning under controlled thermo-hydraulic conditions it is possible to isolate the influence of individual parameters on the cleaning process. This approach has been adopted in this thesis and the development of modelling to describe starch cleaning is presented in Chapter 6.

Chapter 4: Project Development

4.1 INTRODUCTION

This chapter describes the design and construction of an experimental protocol to study the kinetics of starch deposit removal in a flow system under controlled thermo-hydraulic conditions. Suitable measurement techniques for cleaning are appraised from the literature and justification is provided for the selection of the detection methods incorporated. A description of the two rigs developed and the materials used in this protocol is detailed and a review of the apparatus utilised by other workers is given. An outline of the experimental programme which was adopted, together with a description of scouting experiments performed to develop the protocol parameters for fouling and cleaning is described.

A number of unique features of this protocol are worthy of note: It allows the assessment of any aqueous cleaner with the flexibility to determine deposit removal with respect to time from both surface and effluent analysis. In addition, video visualisation provides valuable information on the mechanisms involved during the cleaning process.

A careful analysis on the reproducibility of the experimental data produced using the techniques described for this protocol are also described in this chapter.

4.2 MEASURING METHODS IN THE CLEANING PROCESS

The measuring methods in the literature studied on cleaning technology were classified into **direct** and **indirect** methods by Jennings [1965]. Indirect methods correlate a measurable property of the surface, such as its contact angle or surface tension, with its cleanliness or the amount of soil remaining, whereas direct methods analyse a representative constituent of the soil directly. Corrieu [1981] and Paulsson [1989] made the same classification: either determining the residual soil on the surface or removed soil in the cleaning solution.

However, this classification is still not adequate since it does not provide information as to whether the method is suitable for the recording of dynamic cleaning properties or whether it can be used to determine the cleaning success at a certain point in time. Hence a further classification of these categories into **continuous** and **discontinuous** measuring methods (Kreuzkamp [1994]).

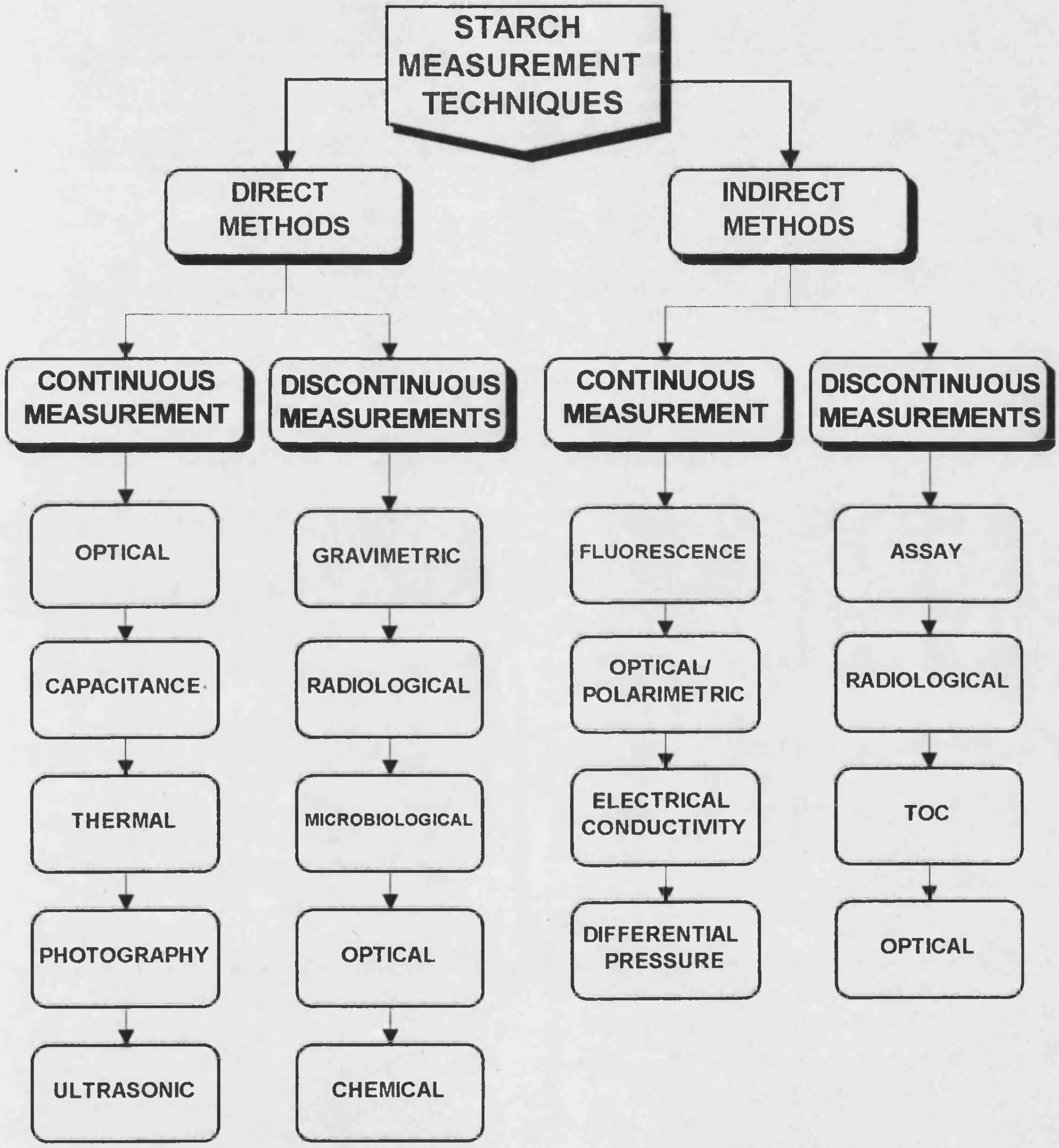


Figure 4.1 Selection of measurement techniques for starch cleaning.

Continuous measuring methods enable the recording of soil removal during the entire cleaning process thus allowing dynamic cleaning processes to be monitored. Measuring intervals of one second are not regarded as discrete. In contrast, discontinuous measuring methods do measure the removal at discrete values of time with a delay. In the extreme case this implies that such methods can only be quantified after completion of the cleaning process.

A summary of the methods applicable for analysing the kinetics of cleaning starch deposits from hard surfaces is described in Figure 4.1. An important criterion chosen for the adopted technique is that it must be accurate, reproducible and determine the starch removal rate over the entire cleaning process.

4.2.1 Continuous Direct Methods

4.2.1.1 *Optical measurement*

One optical method used is ellipsometry. It is based on changes in the phase and amplitude of polarised light on reflection from an interface which are affected by the presence of a thin film on the surface. This method allows the refractive index and thickness of a deposit layer to be determined *in situ* within a time resolution of a few seconds, providing the refractive index of the surface is known. However, the composition of the layer cannot be determined and its use is restricted to smooth reflecting surfaces and transparent media and films. Karlsson *et al.* [1997] has used this direct continuous method to study the adsorption of proteins on metallic surfaces.

4.2.1.2 *Capacitance*

The change in capacitance as a result of a change in dielectric properties can be used to quantitatively determine the removal of deposits on surfaces. Montelius [1988] measured the thickness of adsorbed protein layers on stainless steel surfaces with this method.

4.2.1.3 *Thermal measurement*

A hot-wire anemometer can be used to measure the heat transmission from a surface to the liquid flowing over it. If the surface is soiled, the heat transmission decreases in proportion to the thickness of the soil deposit. Paulsson and Tragardh [1985] used two flush mounted film probes connected to a constant temperature anemometer to measure the removal of deposit in turbulent pipe flow under fully developed flow conditions.

4.2.1.4 *Photography*

Graβhoff [1994] has monitored continuous milk deposit removal from test samples using a video camera. Single video images at different stages of the soil removal process were stored on an image processing PC. These stored images were analysed by a screen pixel count. The digitised results of the soil removal procedure were then presented as a function of time.

4.2.1.5 *Ultrasonic Sensors*

The use of ultrasonics for direct on-line sensing of the build up of fouled films inside pipes has been developed by Withers [1993]. The prototype sensor developed incorporates two transducers; a transmitter and receiver, to transmit the ultrasound across the pipe so that it passes through the pipe walls, product and any fouling present. The drawback with this approach is that the signal will be influenced by the product as well as by the fouling film. It is able to detect the presence of films as thin as 0.1mm and measure film thickness over the range 20^{0}C to 140^{0}C. However, the use of ultrasonic detectors is still in its infancy and a commercially available detector may be some time in the future.

4.2.2 Discontinuous Direct Methods

4.2.2.1 *Gravimetric method*

This method frequently involves the weighing of a substrate before cleaning and re-weighing it subsequently to dry mass i.e. removing any moisture present. For example, the starch adhering to the surface is dispersed in a suitable solvent, precipitated with alcohol, filtered to recover the precipitate and quantitated gravimetrically by weighing the dried starch. Balogopalan *et al* [1988] proposed a gravimetric method for starch estimation in cassava tubers based on dry matter content.

Espig [1997] has applied simple gravimetric techniques to determine the kinetics of oil film removal from stainless steel surfaces using several types of cleaning agents.

4.2.2.2 *Radiological method*

A weakly radioactive isotope is incorporated into the soil as a tracer, and the residual activity detected is used to determine the residual fouling remaining on the surface. This method relies upon the tracer having no effect on the rate of removal of starch and the radioactivity lost from the surface to be a true representation of the whole mass of deposit removed.

Pflug *et al.* [1961] used the tracer ^{32}P to study the depositing and cleaning of skimmed milk fouling. Another isotope, already used by Bourne & Jennings [1961] in cleaning studies on tristearin is ^{14}C. This isotope was also used by Montelius [1988] for the examination of depositing behaviour of proteinaceous soiling.

Due to the hazardous nature of radioactive tracers and the disposal problems associated with them, they have been rejected as a means of measurement in this project.

4.2.2.3 *Microbiological measurement*

Microbiological measurement is based on the detection of micro-organisms on surfaces in contact with the product (Bigalke [1985], Langeveld *et al.* [1994]). The micro-organisms which are applied to the surface together with the test fouling are used as an indicator for the removal of a deposit (McGuire *et al.* [1985], Faille C *et al.* [1997]).

The swab contact method is a well known microbiological measurement technique: a wetted cotton swab is moved over the surface to be examined at a uniform pressure and is rinsed in a nutrient medium. After a length of time the number of microbes contained in the nutrient medium are determined. Timperley [1981] has used this method to study the mechanical effect in the cleaning of pipes of different diameters.

A number of problems are associated with using this form of measurement technique: A major drawback is the large time span required for significant growth of microbes to allow a determination of numbers present (Spenceley *et al.* [1994]). Another problem is that the removal of starch and microbiological soil during cleaning does not occur at the same time or rate and hence the results are of little significance for kinetic work.

4.2.2.4 *Optical method*

This method uses the Beer-Lambert law in which light attenuation caused by an absorbing medium is a function of the thickness of the layer. Tragardh & Bockelmann [1980], used this correlation to examine the mechanical effect on the cleaning of glass tubes. This measurement method was performed prior to and after cleaning.

The use of optical methods for the assessment of starch films produced on metal surfaces is inappropriate. The procedure is inaccurate since it cannot evaluate soil depth. In addition, the detergent solution must be translucent.

4.2.2.5 *Chemical method*

Chemical methods are used to measure certain components of soil residues adhering to surfaces. Linderer & Wildbrett [1994], used chemical methods to quantify residues of starch that had accumulated on glass surfaces.

4.2.3 Continuous Indirect Methods

4.2.3.1 *Fluorescence measurement*

Fluorescence measurement detects the secondary radiation emitted by indicator substances in a test media. The intensity of the secondary radiation allows the determination of concentration curves. Plett [1985] used sodium fluoresceinate as a tracer substance to measure the retention time of cleaning solutions in product paths. As temperature has a strong influence on fluorescence, the temperature must be continuously measured at the same time.

4.2.3.2 *Optical measurement*

In laboratory experiments, Ruiz [1972], showed that the optical density of the solution can be used to measure low milk concentrations (0.01-1%) dissolved in rinse water. Unfortunately, the presence of sodium hydroxide and wetting agents was found to affect the optical density measurement.

4.2.3.3 *Electrical conductivity*

Electrical conductivity is a measure of the ionic strength of the solution. Due to the high ionic strength of most detergents, this method can only be applied to rinsing and pre-rinsing processes rather than to characterise solid residues in a cleaning solution (Nassauer *et al.* [1981]). A further drawback with its application is that the conductivity of a solution is temperature dependent and the compensation for temperature variations is difficult. In addition, the fouling onto the probe surface is commonplace and hence frequent recalibration of the instrument is necessary.

4.2.3.4 *Differential pressure measurement*

Measurement of the pressure drop in pipe systems was used by Sandu [1981] to quantify fouling. A reduced hydraulic diameter and a higher surface roughness cause a pressure drop which can be measured to determine both the removal and the formation of a soil deposit. However, pressure measurements are least sensitive when only small amounts of deposit remain at the end of cleaning.

4.2.4 Discontinuous Indirect Methods

4.2.4.1 *Optical method based on starch-iodine reaction*

The starch-iodine reaction is based on the estimation of the blue-coloured complex formed by the reaction of amylose and iodine. A number of iodo-colorimetric methods have been based on the principle that when a starch-iodine complex is formed there is a shift in the peak of absorption to 600-620 nm. The values of the peaks, i.e. the absorption coefficients, depend on temperature and degree of polymerisation of the starch molecule. A method proposed by Englyst and Hudson [1997] suggests the qualitative and quantitative method for starch estimation based on this principle. The starch extract is complexed with potassium iodide-iodine solution and measurement of absorbance at 605 and 530 nm, which corresponds to the absorption maxima of amylose and amylopectin, respectively. The disadvantage of the above method is that it is not applicable to materials containing dextrins, since there is a significant contribution of the blue colour by dextrins.

A photomeric detection method for absorption at 620 nm was employed by Linderer and Wildbrett [1994] in their work concerning starch residues in the cleaning process.

4.2.4.2 *Polarimetric methods*

The starch is dispersed in a suitable solvent and the starch content is quantitated from the clarified solution by measuring the angle of rotation of the plane polarised light. The most extensively used solvent is calcium chloride (Kennnedy *et al.* [1989]). As a result of the high ionic strength, the starch unfolds without the formation of oligosaccharides or glucose.

The disadvantage with this method is the interference caused by hemicelluloses and other non-starchy polysaccharides, which affect the polarimetric measurements (Padmanabhan and Ramakrishna [1993]).

4.2.4.3 *Enzymatic method*

During the milling of wheat grains a proportion of the starch granules in the flour is damaged by the fracturing of hydrogen bonds between, and covalent bonds within, starch molecules (Mathias *et al.* [1997]). Damaged starch granules absorb more water than undamaged granules and are also the substrate for amylases which provide fermentable carbohydrate that is utilised by yeast in the long term fermentation of bread making process (Planchot *et al.* [1997]).

The main methods for the determination of damaged starch rely on the use of amylases which rapidly hydrolyse damaged starch to reducing sugars (expressed as maltose). These are then determined by titration after reduction of a standardised solution of potassium ferricyanide (AACC [1984]). Gibson *et al.* [1992] published an improved enzymatic method which uses fungal alpha-amylase to digest the damaged starch. The oligosaccharides are then hydrolysed by amyloglucosidase to glucose, which is quantified with glucose oxidase/peroxidase reagent.

There are two important variables for these methods. First, the type of amylase used will influence the nature of the hydrolytic products (Planchot *et al.* [1997]). Alpha-amylases produce glucose, maltose and alpha-limit dextrins, whilst beta-amylases have a more restricted ability to digest starch. They will only cleave to within two to three D-glycosyl residues of alpha-1,6 glycosidic bonds in amylopectin, producing mainly maltose and beta-limit dextrins (Planchot *et al.* [1997]).

The hydrolytic products of digestion by amylases can be studied using High Performance Liquid Chromatography (HPLC) and scanning electron microscopy (SEM). HPLC, linked with refractive index (RI) detection, provides a method for the direct qualitative and quantitative evaluation of simple sugars after incubation of flours with solutions of alpha-amylase (Mathias *et al.* [1997]).

The steps involved in the estimation of starch by enzymatic methods are summarised in Figure 4.2 and include:

a) gelatinization of starch using thermostable alpha-amylase,
b) hydrolysis of the liquefied starch to glucose by amyloglucosidase,
c) estimation of the released glucose molecule, either by titrimetric, colorimetric or enzymatic method.

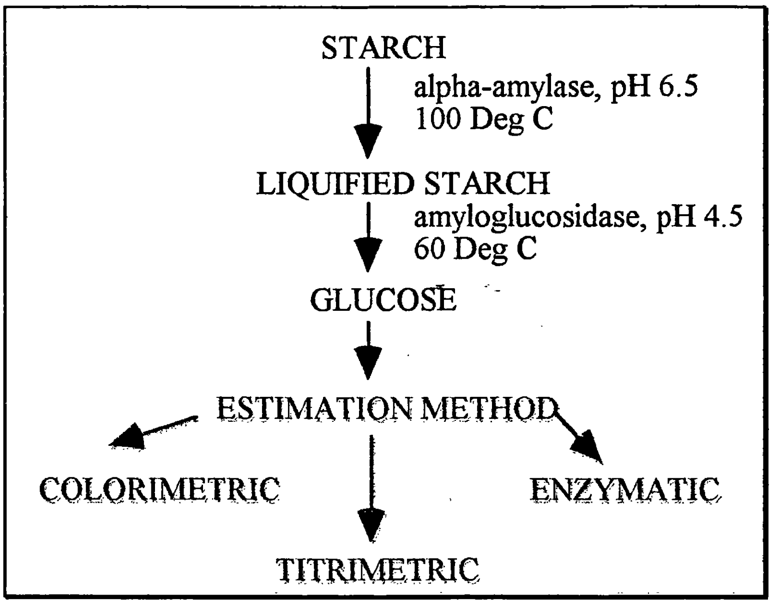


Figure 4.2 Scheme for estimation of starch by enzymatic method.

The greatest advantage of the enzyme method is its specificity. The use of enzymes for starch estimation leads to hydrolysis of the starch molecules and there is no contribution of the reducing sugars from the hydrolysis of the non-starchy polysaccharides.

4.2.4.4 *Total Organic Carbon (TOC) Measurement*

The TOC (Total Organic Carbon) measurement is proposed to be used for the determination of starch dissolved in the cleaning solution. This method has also been employed by Maruyama *et al.* [1991] to measure the rate of removal of starch deposits using a number of cleaning agents.

A Dohrmann DC-180 Carbon Analyser was used in this project. It was capable of analysing samples for TOC, TC (Total Carbon), NPOC (Non-Purgable Organic Carbon) and TIC (Total Inorganic Carbon).

The DC-180 uses an ultraviolet radiation promoted persulphate oxidation and non-dispersive infrared detection of the CO_2 product. The photo-reactor for the instrument consists of a 127 cm x 1.3 mm ID fused silica tube coiled around a low pressure mercury vapour lamp. The volume of the reactor is 1 ml, providing a residence time in the reactor of 7 minutes at a sample flow-rate of 150 μl/min. The UV lamp emits radiation at 184 and 254 nm and the lamp and the photo-reactor are sealed in a gas enclosure. The sample inlet system consists of a 10 ml Luer-lock, a gas-tight syringe and syringe pump operated at a flow-rate of 150 µl/min. The system is sensitive from 10 ppb through to 30000 ppm carbon concentration units. A discussion of the inherent errors associated with this technique are described in Section 4.7.3. The model is guided by a menu-driven video display to establish the analysis modes and parameters. Sample transfer is facilitated by liquid reagent flow and pressurised gas. A typical sequence involves processing of a sample, delivery to the UV reactor for oxidation and then to the NDIR (non-dispersive infrared detector) for measurement of the CO_2 product.

Chemistry of process

The low-temperature UV-promoted persulphate oxidation of organics is summarised as follows:

1. Formation of Main Oxidants

(a) $SO_{4\cdot}^{-} : S_2O_8^{=} + hv \longrightarrow 2SO_4^{\cdot-}$

$SO_{4\cdot}^{-}$ is a very stable and strong free radical oxidising agent.

(b) $\cdot OH : H_2O + hv \longrightarrow \cdot H + \cdot OH$

$$SO_{4\cdot}^{-} + H_2O \longrightarrow SO_4^{=} + .OH + H^{+}$$

2. Excitation of Organics

$$R + hv \longrightarrow R^{*}$$

3. Oxidation of Organics

$$R^{*} + SO_{4\cdot}^{-} + H_2O \longrightarrow nCO_2 + \ldots$$

The carbon dioxide produced can be quantified.

4.2.5 Summary

The literature describes a diverse range of measuring methods adaptable for the cleaning process described in this protocol. Since a central aim of this project was the determination of the kinetics of starch removal, an accurate and quick method was vital. For these reasons, both a direct and indirect method were adopted to suitable cleaning runs. A gravimetric method was employed as the principle direct technique due to its accuracy and TOC measurements were utilised as a secondary indirect method for non-carbon based cleaners.

4.3 WATER SUPPLY

In order to produce sufficient quantities of purified water for use in the make-up of the cleaning solution and rinsing operations, two alternative sources of water were analysed: distilled and reverse-osmosis (RO) purified water. A cost analysis was performed for these two alternatives to determine the most economical solution to provide high quality water for the process. Since an *Elga Intercept RO-5'S'* was available in the Department and the start-up costs and production rate were attractive, this method of supply was adopted. It operates by concentrating the feed stream into a concentrate stream containing most of the dissolved material present in the feed, and a permeate stream which is purified water. Due to an applied pressure gradient, water molecules are forced to migrate from the more concentrated solution to the less concentrated solution. This model can produce a maximum concentrate flow of 450 litres/ hour. The water produced is of a comparatively better quality, in terms of ionic conductivity (30μS) than laboratory distilled water (>100μS).

4.4 CHOICE OF STARCH

Research by Linderer & Wildbrett [1994] shows that the behaviour of a starch film in the cleaning process significantly depends on the type of the soiling starch. The specific properties of the applied starch such as gelatinization temperature, swelling power, solubility and chemical composition are important factors influencing the success of the cleaning process: cereal starches of wheat were found to give much higher residues on hard surfaces than potato starch or chemically modified starch types.

A series of preliminary experiments were conducted using modified potato starch to determine the cleaning kinetics in a static system using an ultrasonic bath. These are presented in Chapter 5. A heterogeneous deposit was produced and the removal behaviour was influenced by this property.

For the study under controlled thermo-hydraulic conditions, a baked wheat starch substrate was used to produce a reproducible and homogeneous deposit onto a stainless steel surface. Two substrate wheat flours were used: Canadian soft and hard breadmaking wheat flour supplied by *Spillers Milling Ltd.*. This flour contains around 70wt% starch and is also rich in 11-16wt% gluten (dry weight).

Table 4.1 summarises the main physical properties of the tested starch types and their components.

PHYSICAL PROPERTY/ COMPOSITION	SOFT FLOUR	HARD FLOUR
swelling power at 95°C	21	18
solubilty at 95°C (%)	41	38
gelatinization temperature (°C)	53-85	53-85
Moisture content (%)	14	13
water binding capacity (g H_2O/ g dry starch)	13	13
crystallinity (%)	36	37
amylopectin (%)	76% starch by difference	76% starch by difference
amylose (%)	23-28	23-28
fat (%)	0.8	0.8
phosphor (%)	0.06	0.06
% protein	11-16	11-16

Table 4.1: Physical properties and composition of hard and soft Canadian breadmaking flour supplied by *Spillers Milling Ltd.*.

4.4.1 Photomicrographic study of wheat starch

A study of the wheat starch substrate used for fouling has been performed using a light and scanning electron microscope. The mode of image formation in transmission microscopical techniques considerably limits the amount of information that can be gained by the use of such techniques. For example, starch granules are translucent under the conditions normally used for light microscopical observation and the superposition of specimen structure at different levels may lead to confusion (Figure 4.3(a)). Also, depth of field limitations at high magnifications result in interference by images which are out of focus with those in focus (Figure 4.3(b)). In scanning electron microscopy the disadvantages of the transmission technique are eliminated and therefore its application to the study of wheat starch technique are eliminated and therefore its application to the study of wheat starch structure, for provision of information complementary to that obtained from transmission microscope studies, is a logical development (Figures 4.4(a)-(c)).

Light microscopy

The starch flour and paste were examined using ordinary light microscopy. Photographs were taken on a 35 mm Kodachrome II film.

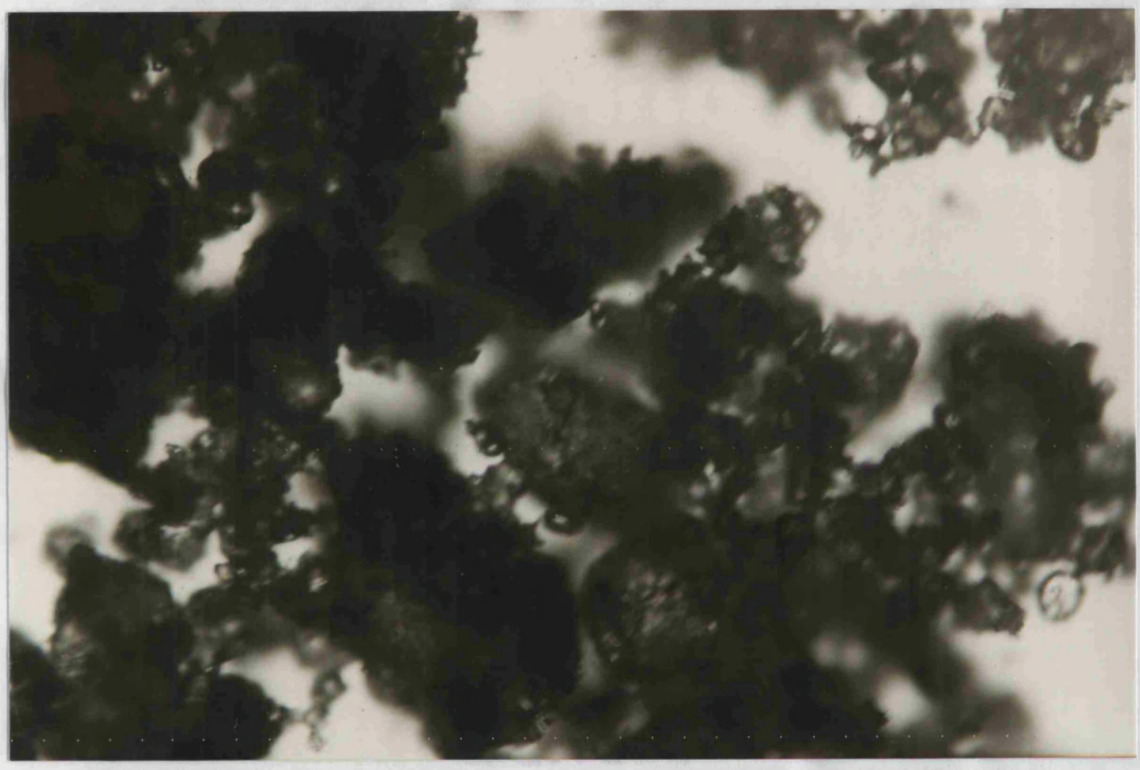


Figure 4.3(a) Photomicrograph using light microscope of Canadian soft breadmaking flour (magnification x 20).

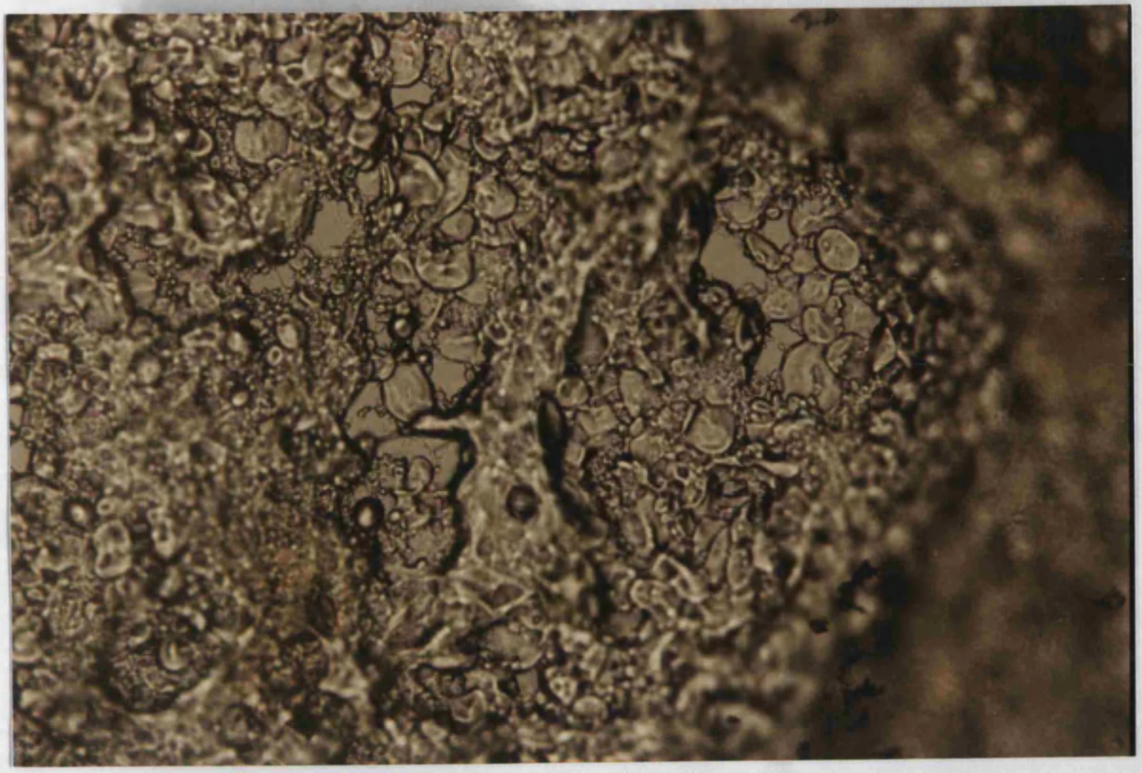


Figure 4.3(b) Photomicrograph using light microscope of Canadian soft breadmaking baked deposit (magnification x 20).

Scanning Electron Microscopy

The air-dried wheat starch flour was mounted on special stubs on a collodion film. The specimen was coated in a vacuum evaporator with approximately 200 to 250A of gold. It was examined using a JSM-T330 scanning electron microscope at 10-kV accelerating potential and photographed on Ilford HP3 35 mm film.

Figure 4.4(a) shows the smooth surface of the starch granules. Figure 4.4(b) shows an equatorial groove on the surface of a granule which appears as a depression rather than a cleft. The large lenticular granules account for over 90 per cent of the total wheat starch structure and the small granules with irregular shapes are found in profusion in the interstices among the large granules (Figure 4.4(c)). A number of damaged granules are seen in these micrographs due to the milling process of the grain.

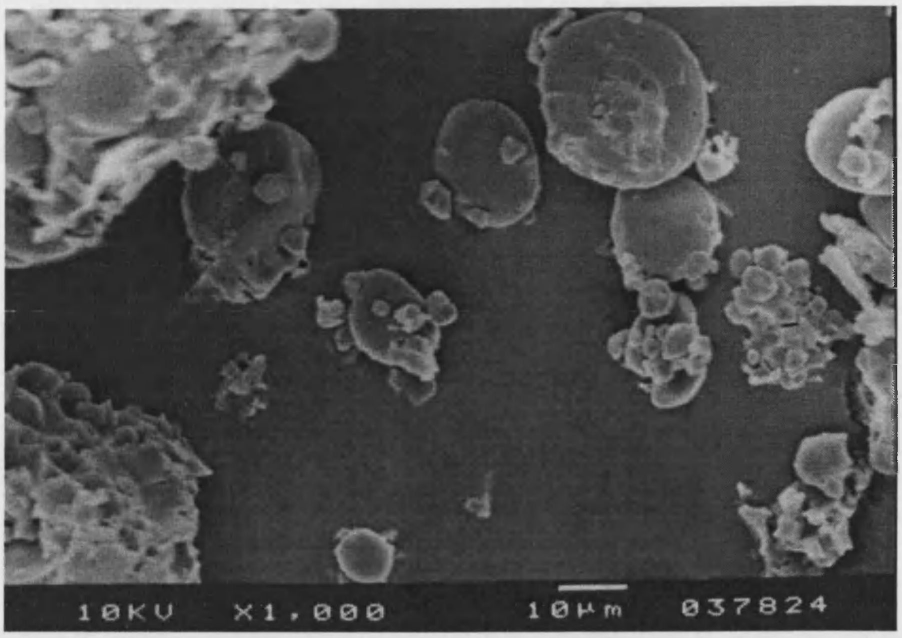


Figure 4.4(a) Electron micrograph of Canadian soft breadmaking flour (magnification x 1000).

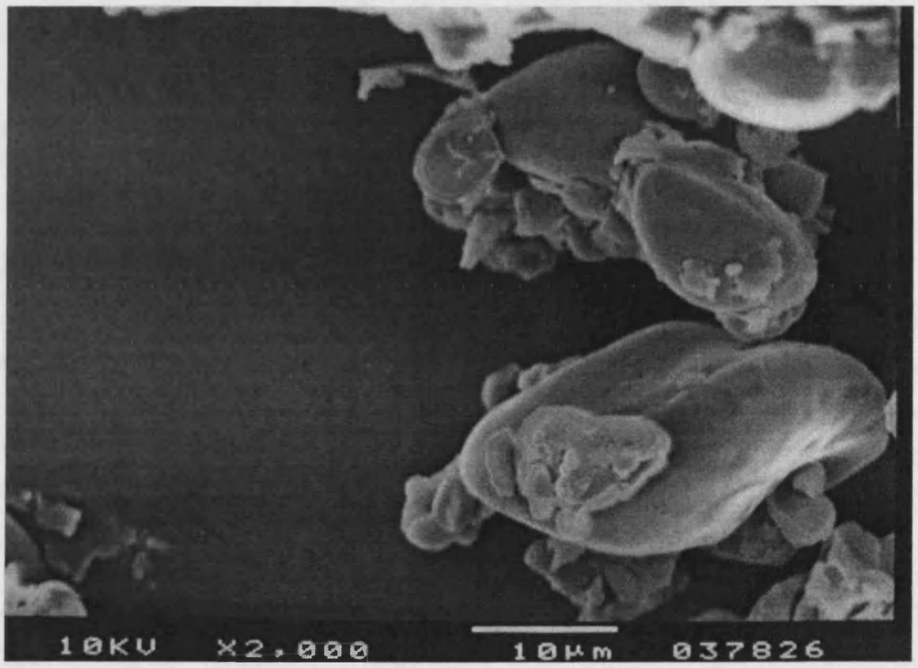


Figure 4.4(b) Electron micrograph of Canadian soft breadmaking flour (magnification x 2000)

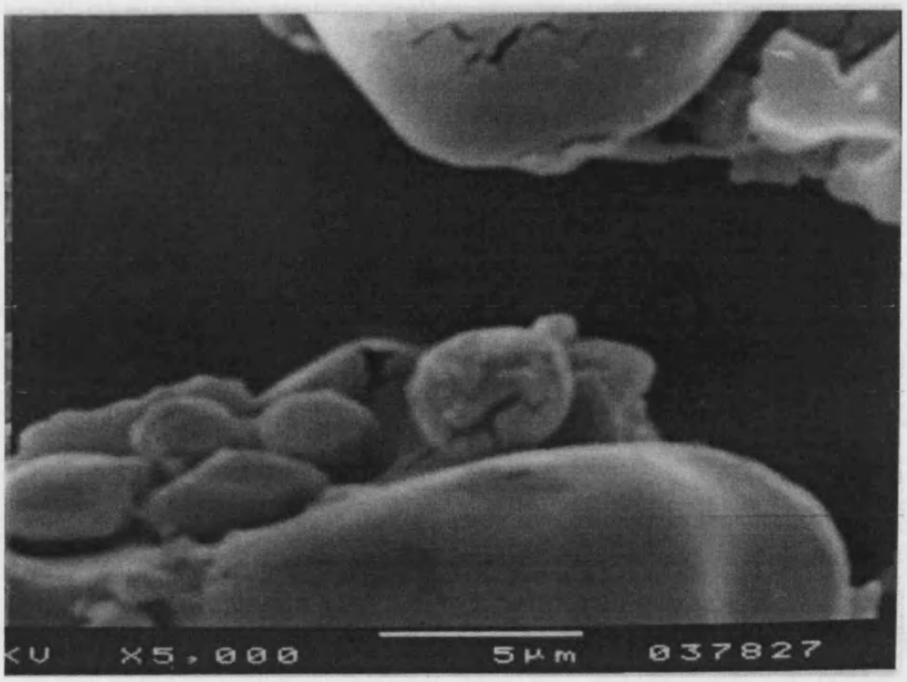


Figure 4.4(c) Electron micrograph of Canadian soft breadmaking flour (magnification x 5000).

The starch component comprises of two polymer constituents: namely amylose (~25%) and amylopectin (~75%). The gluten fraction is a protein matrix representing almost three quarters of the total protein content of the wheat flour. The mechanical properties of a dough made by mixing wheat flour with water are determined by the gluten proteins (Jane [1997]). The two main fractions are the glutenins (comprising of the polymeric prolamins responsible for high viscosity and elastic behaviour) and the gliadins (comprising of the monomeric prolamins contributing to dough plasticity).

4.5 DEVELOPMENT OF EXPERIMENTAL RIGS

In compliance with the factors affecting cleaning discussed in Section 1.5, the experimental apparatus was developed with attention to the mechanical design, operating and system parameters. The apparatus was constructed to produce a uniform and reproducible fouled deposit from a system which is fully understood and subsequently clean under fully defined thermo-hydraulic conditions.

Several stages were involved in this experimental procedure and these are summarised in Figure 4.5. Two rigs are incorporated into this study: namely the fouling (stages 2-3) and cleaning rig (stages 4-5).

4.5.1 Test Piece Design

A rectangular test plate geometry was chosen for the design since it allowed the control of process variables, whilst allowing flow visualisation within a glass cell. The dimensions of each plate were standardised: 23 mm wide, 150 mm long, 3.5 mm thick with a channel ground through the centre line, 6 mm wide and 2 mm deep (Figure 4.6(a)-(d)). This geometry had been selected in the design to enable the minimisation of edge shear stress effects during the cleaning process within a flow system (Ramachandra and Spalding [1976]). The plates had been fabricated to the same machine-polished finish (Ra=0.009 mm). Figure 4.6(e)-(f) depict the surface roughness of the groove in a clean stainless steel test-plate as viewed using a scanning electron microscope (Model 6310, accelerating voltage 15kV). Details on the roughness tests performed on each plate are given in Appendix A1. A smaller number of plates were also fabricated to a similar specification but with the channel 3 mm deep; these were used to investigate the effects of deposit thickness on the removal behaviour.

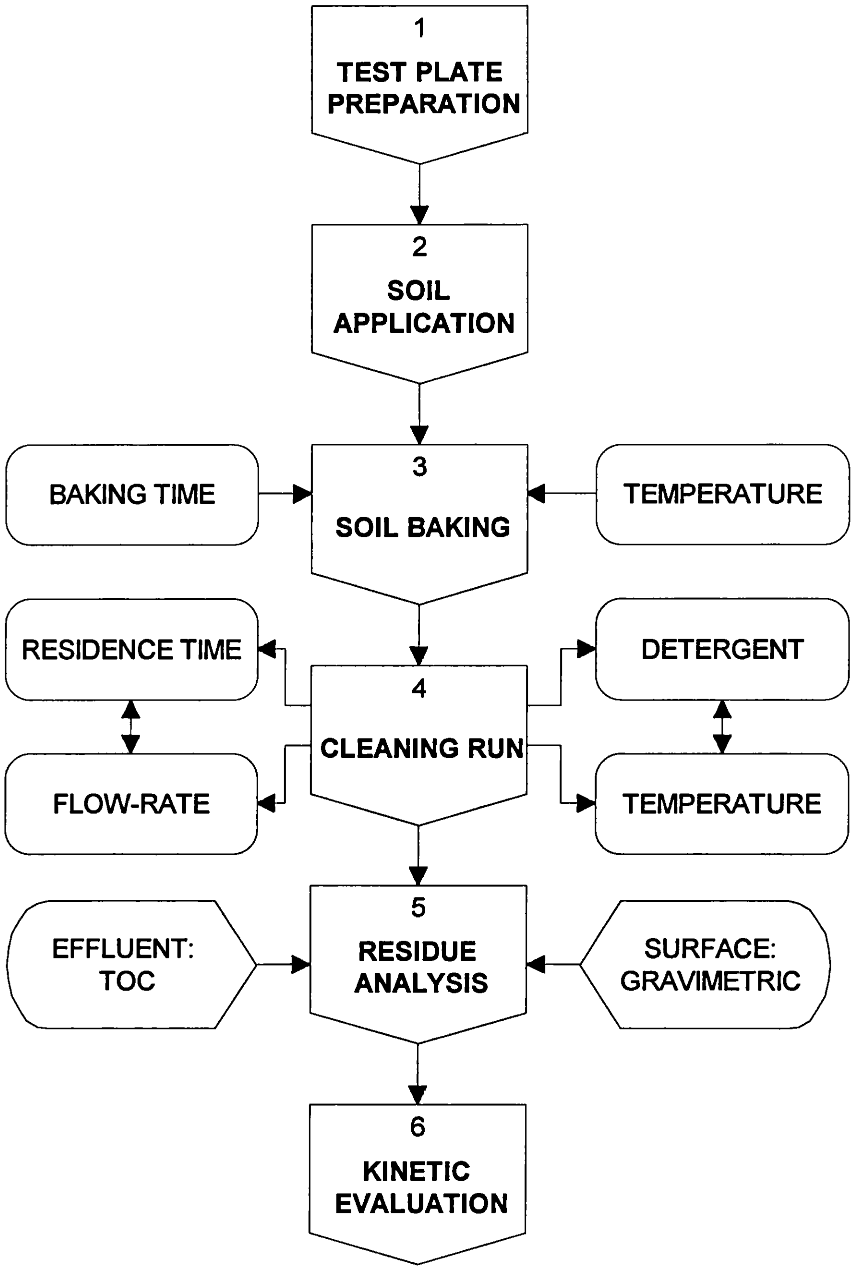


Figure 4.5 Flow diagram of experimental procedure and process relationships.

In order to provide a comparison between different cleaning conditions and agents it was necessary to ensure that the stainless steel plates used were 'clean'. The term 'clean' is taken by food sanitarians to mean "completely free" of soil residues from preceding or extraneous contamination (Harper, [1972]). To ensure this level of cleanliness, (Stage 1, Figure 4.5), each plate was cleaned in a 4.5 litre thermostatically controlled ultrasonic bath (*Decon*) containing a neutral ultrasonic detergent at 60°C for 30 minutes and then rinsed and dried prior to use in the fouling apparatus.

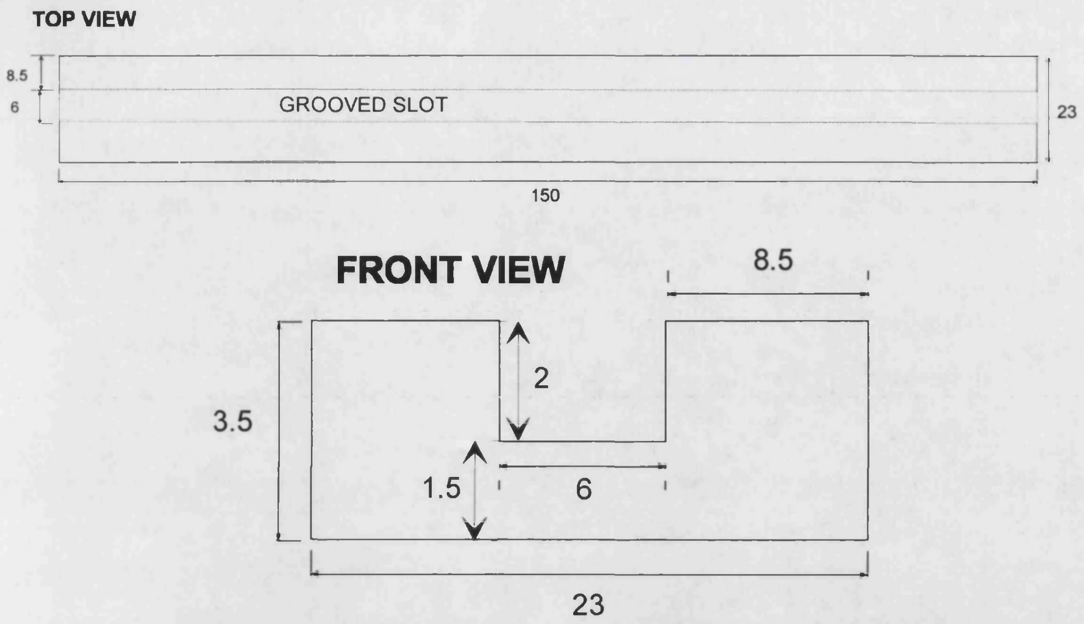


Figure 4.6(a) Schematic diagram outlining dimensions of designed test-plates (all dimensions in millimetres).

Figure 4.6(b) Top view photograph of test-plate fabricated with a 2 mm depth groove

Figure 4.6(c) Side view photograph of test-plate fabricated with a 2 mm depth groove.

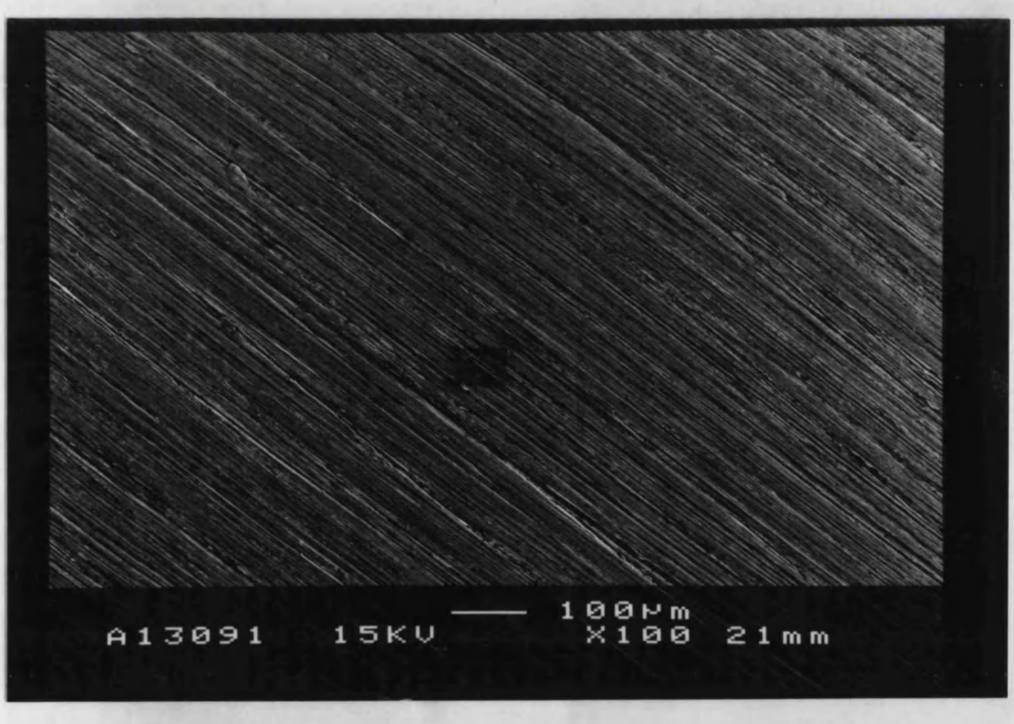


Figure 4.6(d) Photomicrograph using Model 6310 scanning electron microscope of the groove in a clean 316 stainless steel test-plate (magnification x 100).

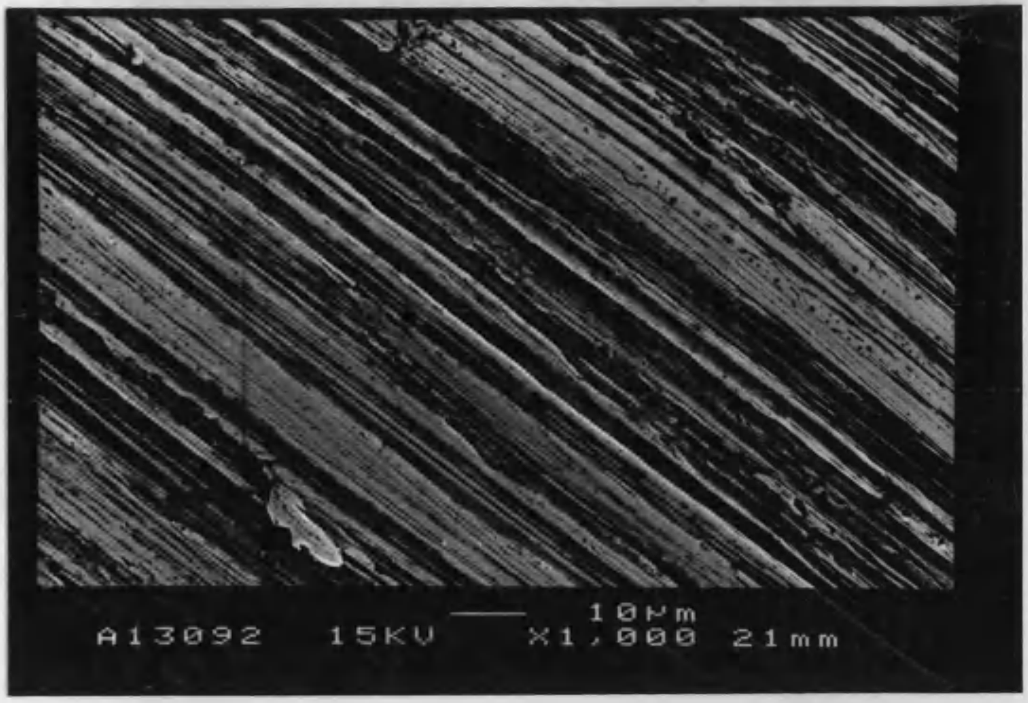


Figure 4.6(e) Photomicrograph using Model 6310 scanning electron microscope of the groove in a clean 316 stainless steel test-plate (magnification x 1000).

4.5.2 Materials of Construction

A number of factors related to the operating conditions for the rig had to be considered in the selection of the most suitable material for construction. The most demanding possible operating conditions foreseen were a temperature of 90^{o}C, flow-rate of 6 l/min and concentrations of sodium hydroxide or nitric acid of 20wt%.

Hence, the most important factors in the material selection must take into account were:

- Mechanical properties of the material: strength; effects under operating temperature conditions; stiffness; corrosion resistance.
- Ease of fabrication: welding, joining lines etc.
- Availability in standard sizes.
- Cost.

By use of corrosion data in Perry's [1973], a preliminary screening of materials was conducted for these "worst" operating conditions. It was found that tin, lead, brass, aluminium and mild steel were unsuitable. Stainless steel, polyethylene and glass were used as alternatives. The advice of technical service departments of the companies supplying equipment was also sought to ensure compatibility before purchase. All stainless steel fittings used in the cleaning rig were obtained from *Swagelok Ltd.*

4.5.3 Experimental Apparatus

4.5.3.1 Fouling Rig

Equal weights of Reverse Osmosis (RO) water and wheat flour were mixed using an electric stirrer to produce a well-mixed paste of even consistency and viscosity. This paste was then applied to the channelled groove of a 316 stainless steel test plate. Excess paste from the channel was scraped away from the test plate surface using a stainless steel knife edge, leaving a uniform foulant layer, 2 mm thick. The test plate was then transferred to a fan-assisted oven at 180°C for a residence time of 10 minutes (Stage 3, Figure 4.5). These conditions had been chosen to simulate industrial baking conditions whilst ensuring a tenacious but reproducibly baked deposit is formed. A typical plot for the temperature profiles existing during are fouling run are presented in Figure 4.7(a). In this profile, Type K thermocouples were placed in the oven at two strategic points, whilst a Type K thermocouple was attached using a heat resistant adhesive tape to the surface of the test plate and a hypodermic Type T thermocouple was fixed into the channel housing the applied paste, prior to baking. The test plate was then allowed to cool under ambient conditions in a desiccator, to minimise water absorption, before weighing the plate and baked deposit to an accuracy of ±0.001g using a *Sartorius* balance. The temperature profile for the overall process is depicted in Figure 4.7 (b).

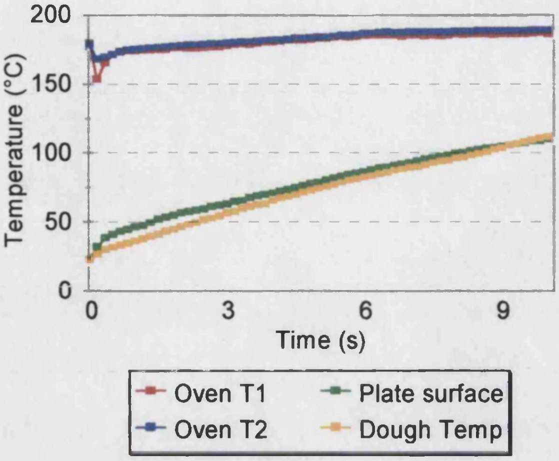


Figure 4.7(a) Baking profile during a typical fouling run.

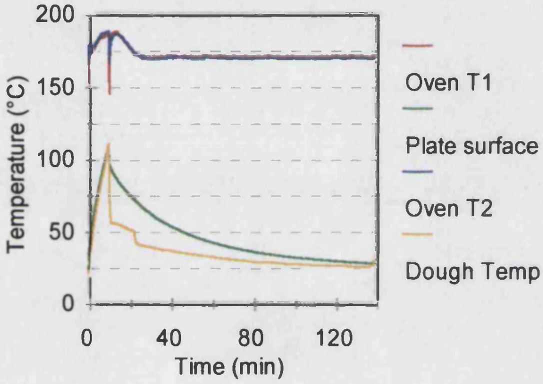


Figure 4.7(b) Overall temperature profile during a typical fouling run.

4.5.3.2 Cleaning Rig

Photographs of the cleaning rig and the table layout are depicted in Figures 4.8 and 4.9 respectively. A simplified flow diagram of the cleaning rig is given in Figure 4.10. The cleaning rig has been designed and constructed from scratch. A paramount consideration in the rig design was safety during operation since a number of potentially dangerous cleaning solutions would be used.

The design is versatile: allowing the of cleaning fouled plates individually, whilst providing precise control of thermo-hydraulic conditions. Continuous monitoring of individual variables (temperature, flow-rate, pH and pressure), affecting the cleaning process was possible by means of an 18 channel portable data-logging facility (1253 series *Squirrel Instruments*).

For each run, cleaning solution was first prepared in a 200 litre storage tank enclosed in a perspex shielded bund. The chemical cleaner formulation was added to the tank in either solid or liquid form and completely mixed by an overhead electric stirrer, until completely dissolved. This cleaning solution reservoir was heated to the required process temperature using a thermostatically-controlled oil heater (Model 18-200, *Conair & Churchill Ltd.*). It consists of six 3kW heaters capable of operating the unit to a maximum temperature of 200°C. The unit consists of a "one-piece" welded assembly of stainless steel chambers which are interconnected and thermally insulated. These chambers house heavy-duty electric heating elements which are switched on and off automatically by solid state electronic control systems and also by use of "high" and "low" levels of heater output operated by touch controls. This heater was connected via an insulated oil line circuit, consisting of ½" 316 stainless steel tubing to the cleaning tank. A helically wound oil line was seated within the cleaning tank to ensure good heat transfer characteristics. Accurate temperature control of the cleaning solution was possible by means of a feedback control loop using a Type K thermocouple probe (± 0.5°C) linked to a digital display for control between ambient conditions to a maximum of 90°C.

The pH of the cleaning solution was measured using a probe situated within the cleaning reservoir tank. It was continuously monitored via an analogue output signal from a pH meter connected to the data-logger, during each cleaning run.

The solution was pumped by a chemically-resistant magnetically coupled centrifugal pump (P-01, *Little Giant, Model TE-7MD-HC*). The flow-rate was monitored by an electromagnetic flowmeter (Picomag II DMI 6533, *Endress & Hauser*) and controlled through a fine control needle valve (V-07). The flowmeter chosen offers a great deal of versatility in terms of programmable functions including the production of an analogue output signal over the flow-rate range 0-20 $dm^3 \ min^{-1}$ for data-logging purposes. In addition, the flexibility of this unit will allow future investigations on the effects of pulsatile flow on cleaning for which little reported work has been cited in the literature.

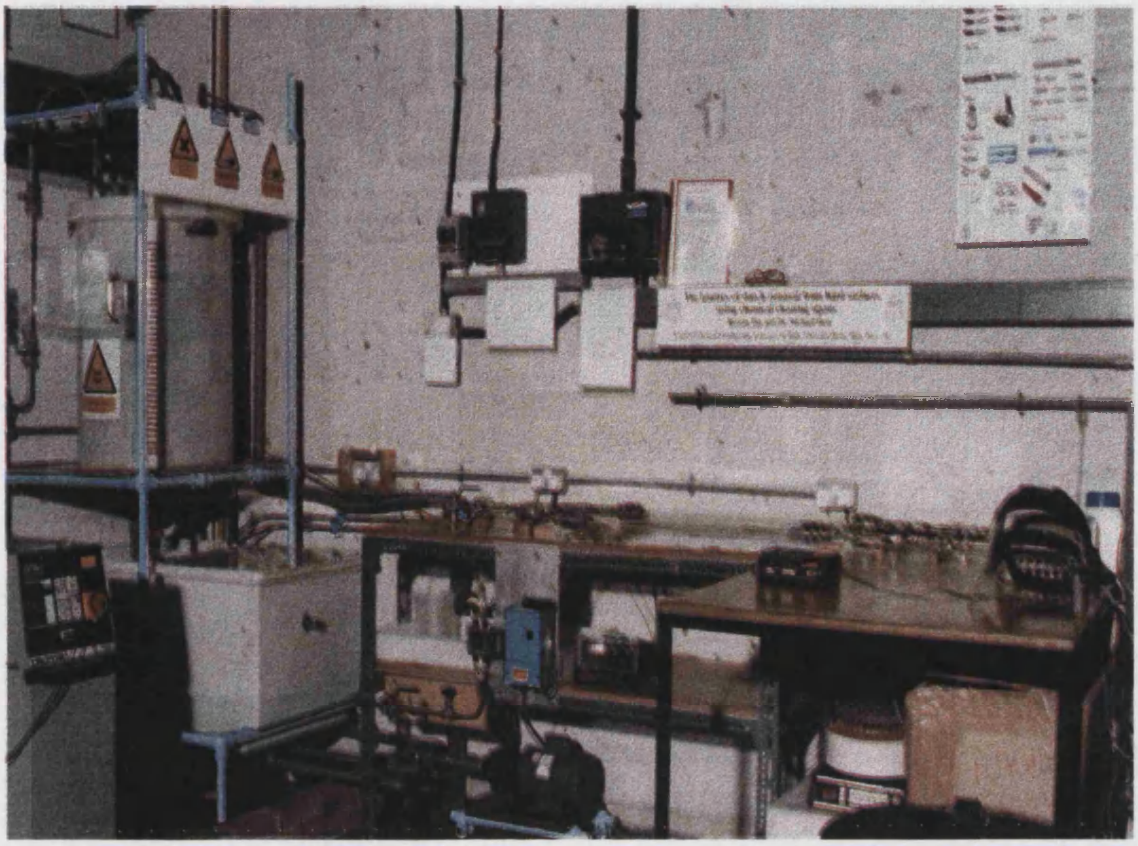


Figure 4.8 Photograph of the Cleaning Rig.

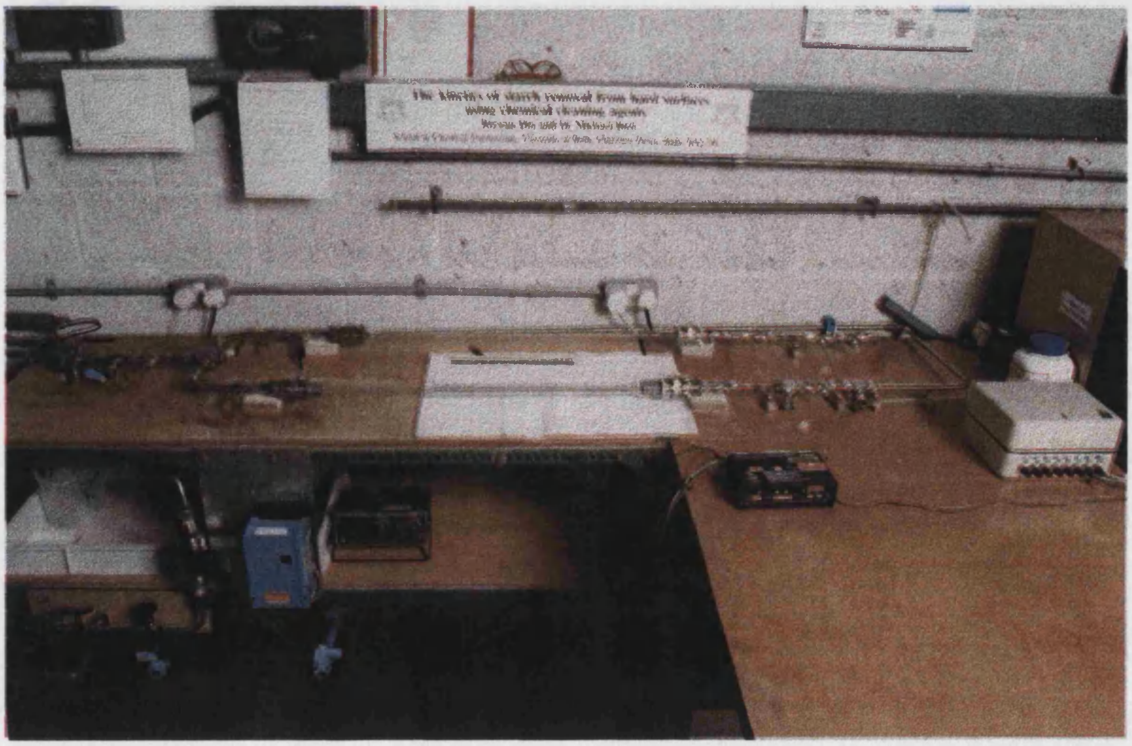


Figure 4.9 Table layout for glass cells containing test-plates used for cleaning.

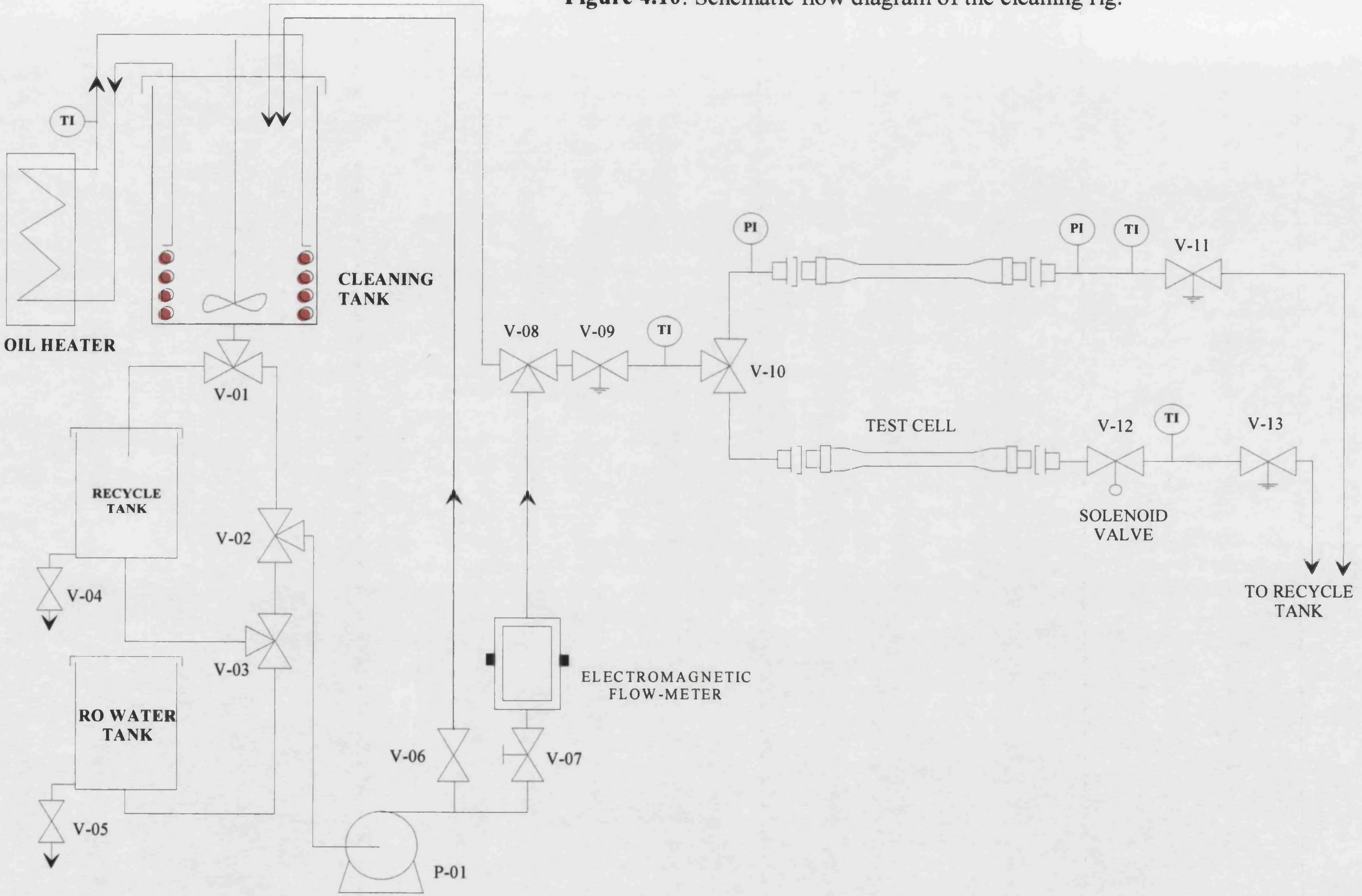


Figure 4.10: Schematic flow diagram of the cleaning rig.

The solution was circulated through a ½" (6.35 mm) stainless steel pipe loop circuit until the desired temperature and flow-rate conditions were achieved. Flow was then diverted by means of a three-way valve system (V-08) into one of two parallel networks where the test plate was mounted.

The test-plates were mounted within the main process stream inside rectangular cross-sectioned glass cells (supplied by *Norlab Glassblowing Ltd.*). This geometry was chosen to aid the visualisation of mechanisms observed during the cleaning process without leading to optical distortion as apparent in circular systems. Video and still pictures of the cleaning process were recorded (see Chapter 5). The ends of the glass cells had been drawn out into 1½"circular cross-sections to enable connection via *Swagelok* ultra-torr fittings to the ½" process tubing. These ultra-torr fittings had viton O-rings which formed a compression fitting onto the ends of the test cell. The temperature and pressure profile across the test cells were monitored during the cleaning run by calibrated Type T thermocouples and pressure transducers (*Druck Ltd.*) and readings were subsequently data-logged.

In order to ensure flow pattern uniformity of cleaning agent over the test plates, a stainless rectangular bar (23 mm wide, 300 mm long, 3.5 mm thick) was included within the glass cell as a lead-up piece, adjacent to the inserted test-plate.

The effect of a range of cleaning agent concentrations and temperatures were studied for run times of 25 minutes. This range was chosen to cover all but the most extreme industrial cases. Both turbulent and laminar flow-rate characteristics were studied for the effective cleaners.

The cleaning solution passing over the test plates was collected in the recycle tank (see Figure 4.10). Samples of bulk effluent could be regularly collected in 20ml borosilicate glass tubes using a *Pharmacia Redifrac 100* carousel fraction collector, by means of a timer feedback control system actuating a solenoid valve (V-12). These samples could then be later analysed for soil by means of a *Dohrmann* Total Organic Carbon (TOC) analyser. Using this method, an injected sample was oxidised by the TOC to form CO_2 which was proportional to the amount of carbon in the sample (Section 4.2.2.4). This technique measures the amount of organic carbon in the solution down to concentrations as low as 10ppb. However, this approach could only be used for non-carbon based cleaners; otherwise the high carbon background count from the detergent would occlude the soil concentration reading.

A gravimetric technique was also used to provide an assessment of the direct removal kinetics from the stainless steel test plate surface. Test plates removed after set cleaning times were oven dried at 50°C to constant mass and the residual soil content determined by use of the *Sartorious* balance. This enabled a kinetic profile to be drawn for the cleaning process as well as providing a comparison between the overall cleaner effectiveness. Graphs of the removal characteristics for each cleaner are presented in Chapter 5.

All acidic and alkaline cleaning solutions were neutralised before discharging to the mains drain.

4.6 DEPOSIT CHARACTERISTICS

The fouling conditions adopted for the majority of the experiments performed have already been described in Section 4.5.3.1. This section will outline an investigation into the deposit characteristics and properties. A number of factors were considered including the foulant uniformity, baking time, deposit thickness and composition.

4.6.1 Determining a Reproducible Deposit

A number of scouting experiments were performed to determine suitable and reproducible fouling conditions. An industrially relevant baking temperature of 180°C and a residence time of 10 minutes were adopted; providing the most suitable operating parameters under the maximum cleaning time of 25 minutes used.

A number of variations in the quantity of added water to both soft and hard Canadian breadmaking wheat flour (supplied by *Spillers Milling Ltd.*) required to produce a paste for application to the test plates were also examined. From the results, a 50-50wt% mixture of water and soft Canadian breadmaking flour was found to produce the best substrate and be most suitable in terms of producing a measurable cleaning efficiency in the time span considered.

4.6.2 Texture Analysis

Three representative fouled samples using the protocol described were tested using the Stable Micro Systems TA.XT2. All three were subjected to the same experiment, which involved pushing a 3 mm flat-ended cylinder probe into the sample by a distance of 2mm at a speed of 0.5 mm/sec. The cylinder probe is used for puncture and penetration tests on samples and loadcell measurements are recorded to determine the fracturability of the samples. The data acquisition rate was set to 200 points per second, so a total of 400 measurements were made during the course of the test. The force required for penetration was measured and the speed was controlled. Sample results are given in Table 4.2 and Figure 4.11.

Sample Number	1st peak fracture mass (g)	Max Mass (Hardness) (g)
1	5945.1	7837.0
2	5734.9	7325.5
3	5553.4	8162.7
4	5540.0	7883.2
5	6104.6	7239.1
Average	**5775.6**	**7689.5**
Standard Deviation	**246.7**	**393.2**

Table 4.2: Measurement of fracturability and hardness of 2mm depth sample wheat deposits using a Stable Micro Systems Texture Analyser TA.XT2.

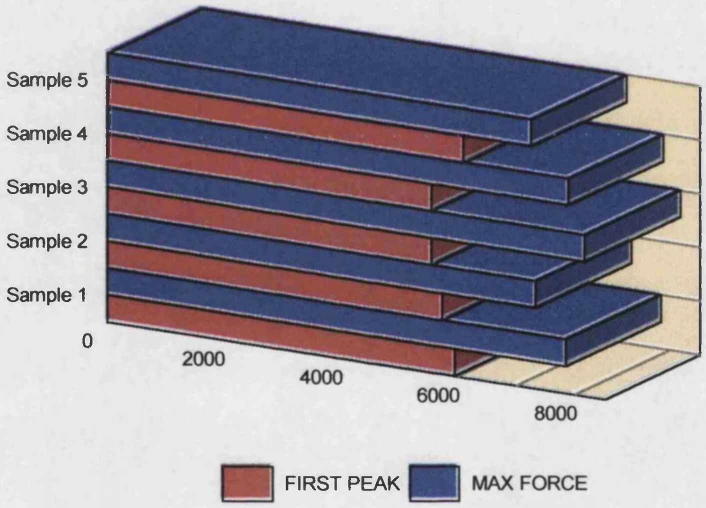


Figure 4.11: Comparison of maximum and first peak forces required to fracture 5 wheat starch deposit samples contained in 2mm depth test plates.

An observation from the results indicates that there is little variation in hardness along the strip of deposit and the preparation technique yields relatively uniform deposit layers in terms of their fracturabilty and hardness, within the boundaries of experimental error (Figure 4.11).

4.6.3 SEM study of deposit

The structure of the 2mm wheat starch deposit, produced under the conditions described previously, was studied using scanning electron microscopy to determine the changes caused by the baking process. Dried samples were stuck to SEM discs using a conductive paste and were then splutter coated with a thin layer of gold to minimise artefacts produced due to bombardment with electrons using a JSM-T330 Scanning Electron Microscope, in the Electron Optics Centre, University of Bath. An operating voltage of 10kV was used for imaging and photographs are presented in Figures 4.12(a)-(f).

The photographs indicate that the surface consists of an undulating matrix with a network of cracks between the aggregates. The morphology of the deposit appears to change with relative depth of deposit studied: closer packing of starch granules and foreign matter (believed to be protein) was observed at increasing depths (Figures 4.12(d)-(e)). The sagittal section, Figure 4.12(f), depicts the close-packed matrix of deposit below the surface and Figure 4.12(g) indicates the characteristic packing patterns observed at these depths: the extent of starch granule deformation and associated foreign matter was more than at the surface.

Since it is well established that the changes that occur in starch granules are a function of both temperature and water availability (Hoseney [1984]), it indicates that the degree of gelatinization observed by granule deformation is greater at increasing depths of the deposit. This may be explained in terms of the increasing water availability required to initiate gelatinization and pasting, at lower depths due to a high evaporation rate from the surface of the deposit.

Figure 4.12(h) was imaged using the Model 6310 at an accelerating voltage of 15kV: it indicates a smooth matrix deposit is attached to the underlying stainless steel substrate; indicating a heterogeneous deposit is formed during baking.

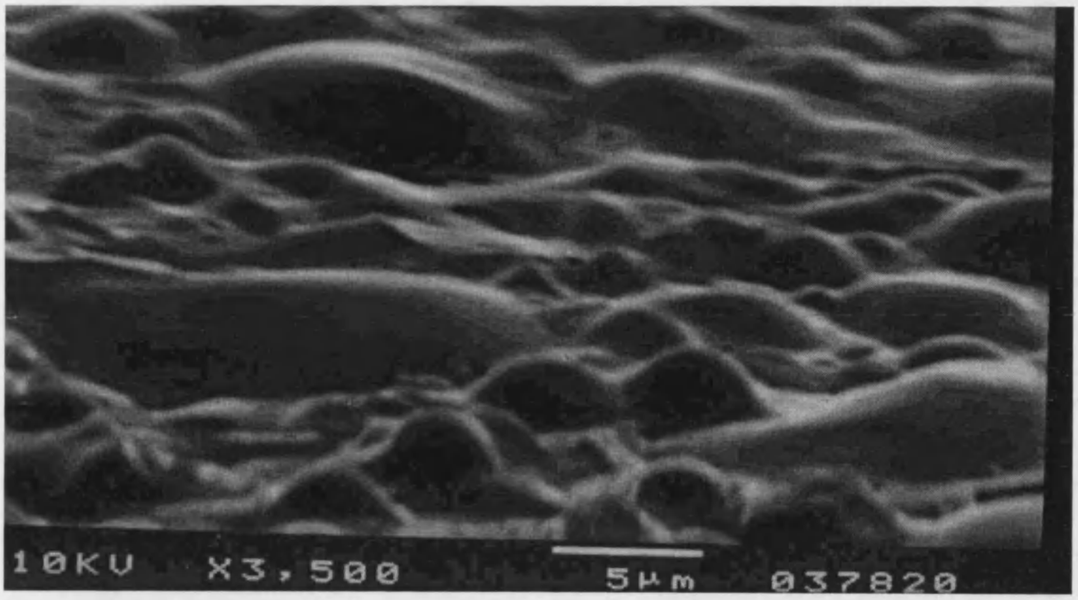


Figure 4.12(a): Electron micrograph of baked wheat deposit surface (magnification x 3500).

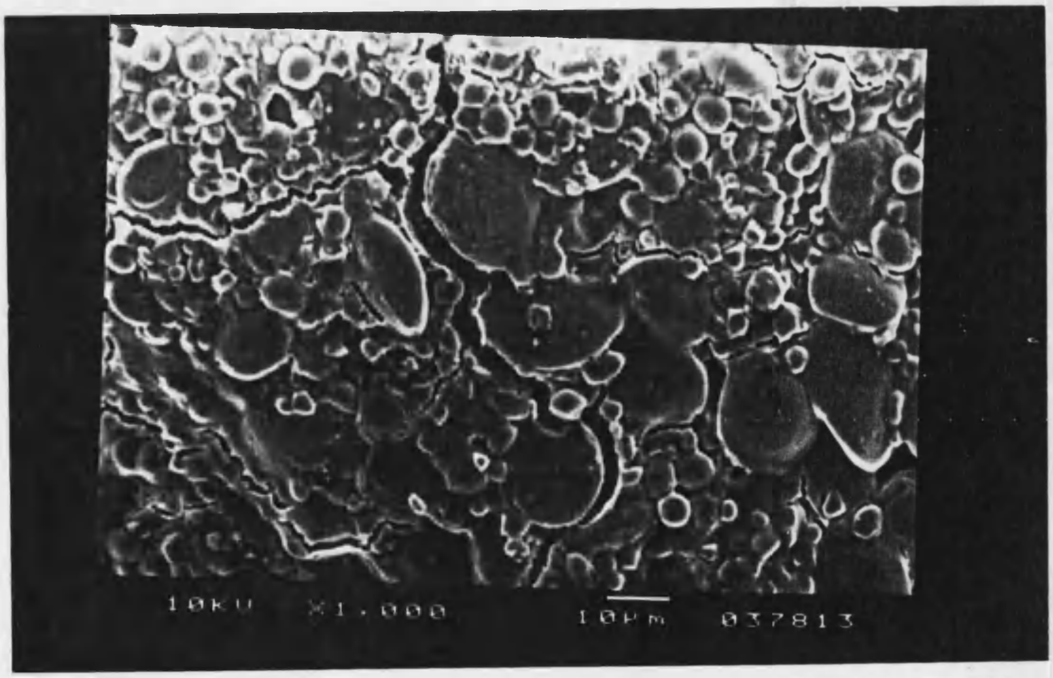


Figure 4.12(b): Electron micrograph of baked wheat deposit surface: top view (magnification x 1000).

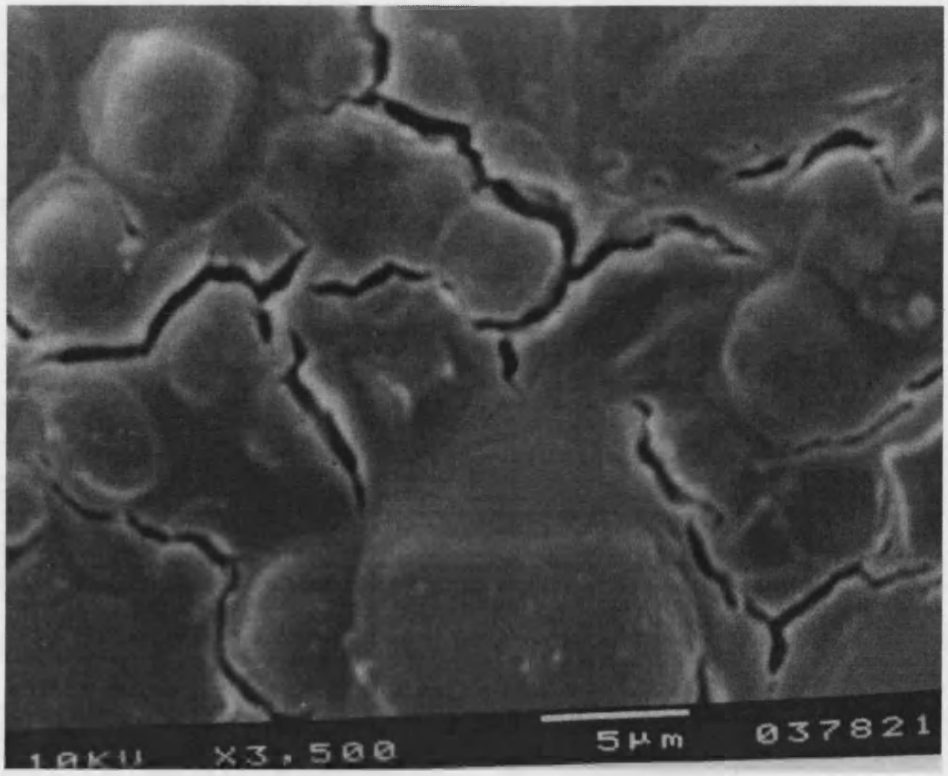


Figure 4.12(c): Electron micrograph of baked wheat deposit surface: top view (magnification x 3500).

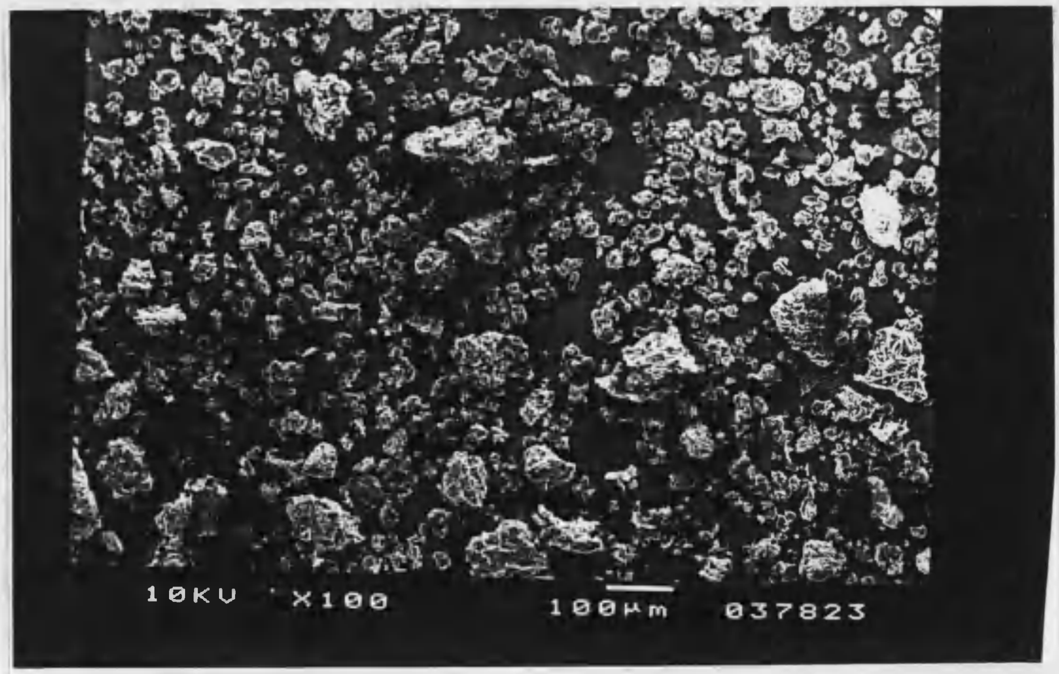


Figure 4.12(d): Electron micrograph of baked wheat deposit surface: top surface layer (magnification x 100).

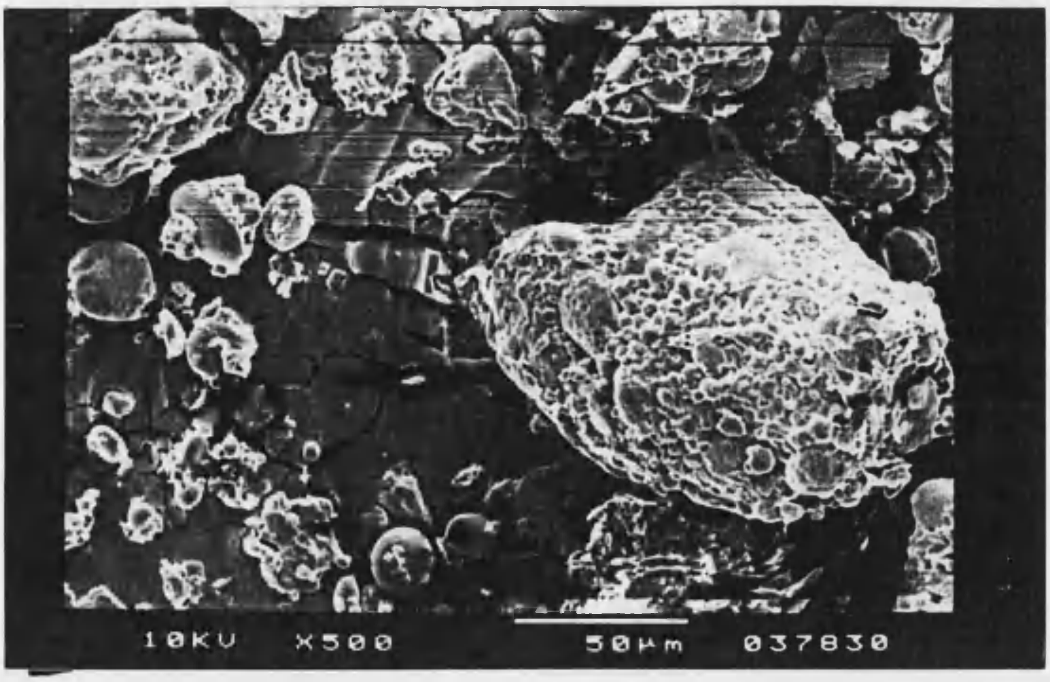


Figure 4.12(e): Electron micrograph of baked wheat deposit surface: top surface layer (magnification x 500).

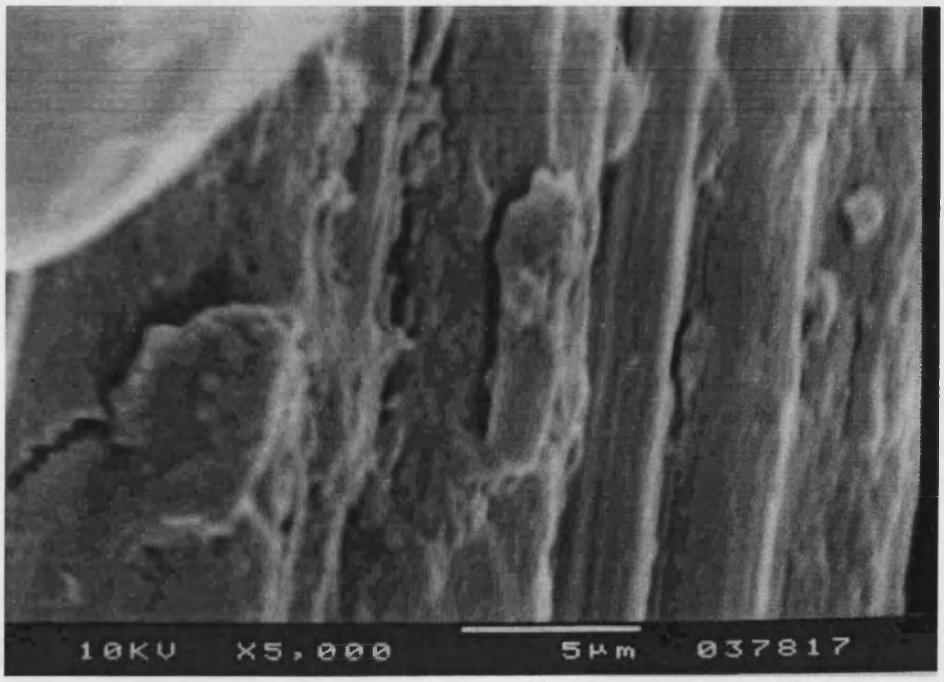


Figure 4.12(f): Electron micrograph of baked wheat deposit surface: sagittal view (magnification x 5000).

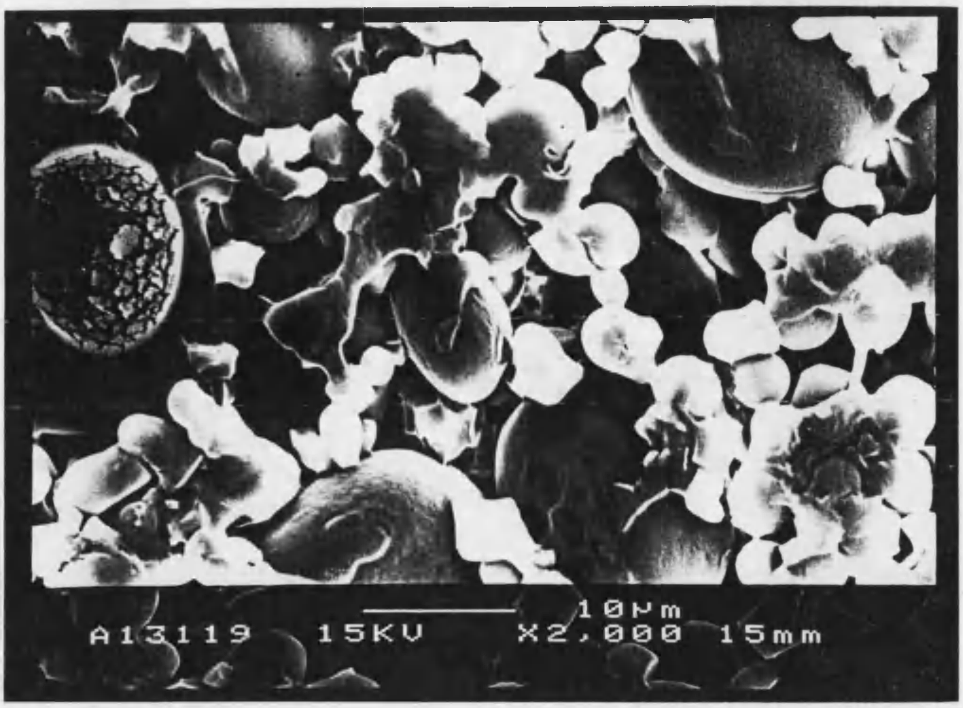


Figure 4.12(g): Electron micrograph of baked wheat deposit: close packing and deformity of starch granules due to gelatinization apparent (magnification x 2000).

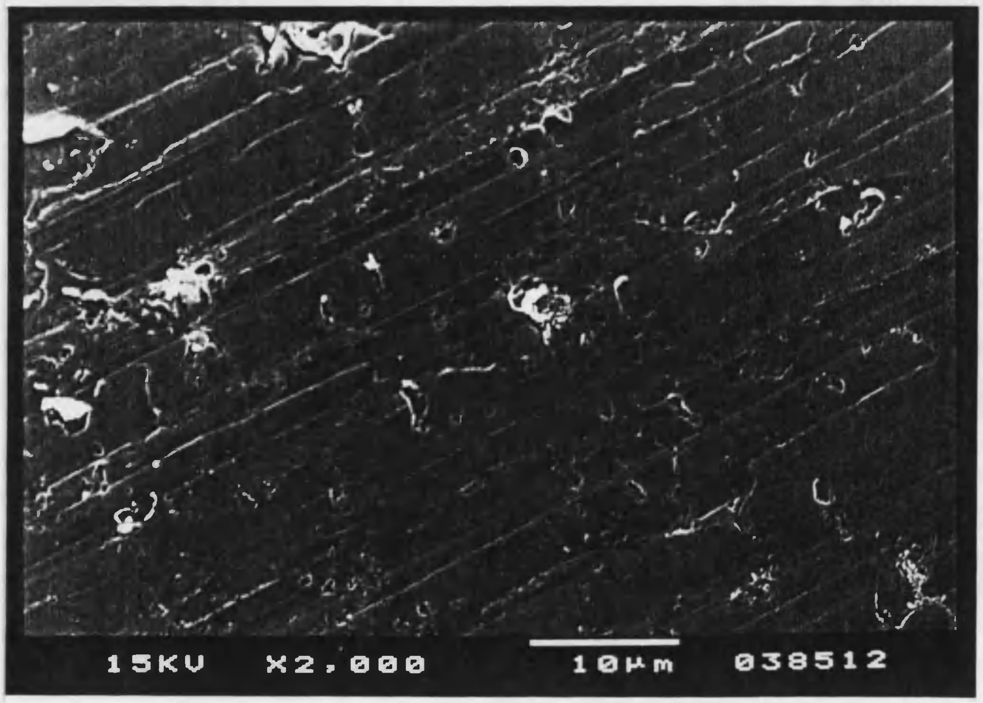


Figure 4.12(h): Electron micrograph of baked deposit surface: proteineous base layer adhering to stainless steel substrate(magnification x 2000).

4.7 EXPERIMENTAL ERROR ANALYSIS

4.7.1 Total Error Analysis

An inherent part of experimental data is a degree of scatter in the results obtained. It is however, important to identify the areas in an experimental protocol which lead to the sources of error. The errors can be classified into two types; random and systematic. The former can be caused by equipment or operator deficiencies and can be decreased by repeating the experiment. In comparison, systematic errors can be corrected by the re-calibration of equipment used for experimentation.

Repetition of experimentation yields a global error estimate for the protocol. Three separate removal runs were performed using alcohol ethoxylate at 4l/min and 60°C for a total cleaning time of 25 minutes (Figure 4.13). An explanation for the anomaly high readings at 5 minutes compared to 10 minutes in Figure 4.13 may be due to the that inherently random processing resulting in aggregate removal of deposits. All three cleaning runs were performed at 6 set cleaning times and an analysis of the statistical data is presented in Table 4.3. The global error will be taken as the largest error determined (±17.7%) and be considered to be valid for all experimental data points presented in this thesis. This global error can be traced to three origins; namely: fouling experiments, cleaning experiments and cleaning analysis and these will be discussed in the next few sections.

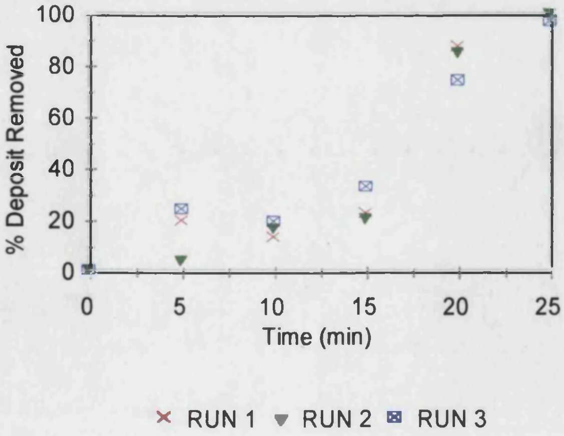


Figure 4.13: Error assessment: three experimental runs at 4l/min 4wt% alcohol ethoxylate, 60°C.

STATISTIC	RUN 1	RUN 2	RUN 3
Standard Error	17.20	17.66	14.97
Standard Deviation	42.15	43.27	36.68

Table 4.3: Statistical data arising from sample experimental runs.

4.7.2 Fouling Experimental Errors

Fouling errors could have several origins:

1. Inconsistencies in the wheat flour deposit and its treatment prior to fouling.
2. Changes in fouling conditions during experimentation.
3. Variations in test-plate surface properties.
4. Variations in deposit mass and uniformity.
5. Treatment of the fouled deposit prior to cleaning.

Measures were taken to minimise errors arising from all these identified sources:

1. All the soft breadmaking flour originated from one 30 kg sack supplied by *Spillers Milling Ltd.*. This bulk sample of flour was stored in an air-tight sealed bin to minimise moisture intake. Hence, flour variations can be assumed to negligible. The flour paste mixed for the fouling protocol was used immediately on production for application onto the test-plates.
2. The accurate control of fouling operation conditions was imperative to provide a valid comparison between experimental runs. Accurate control of baking conditions (±0.5°C) was possible by means of a thermostat controlled fan-assisted oven. Monitoring of process conditions was continued using Type K thermocouples placed within the oven to ensure uniform conditions persisted during the baking cycle. Each of these baking runs were logged using the *Squirrel* data-logger enabling a temperature profile comparison between fouling runs (Section 4.5.3.1) and ensuring uniformity (±17% variation limits).
3. Regular inspections were made on the condition of the fabricated test-plates. Roughness values for the groove were compared between each plate to ensure uniformity.
4. Test plates which showed any significant variation in deposit mass or uniformity were discarded (Section 4.6).

5. After fouling the soiled stainless steel test plates in the oven, they were stored in a dessicator to minimise water absorption. This storage time was kept to a minimum to reduce the effects of deposit ageing.

4.7.3 Cleaning Experimental Errors

The main sources of error are likely from:

1. Preparation of cleaning solutions.
2. Variation in process cleaning conditions.

Measures were taken to minimise these identified sources of errors:

1. Cleaners used for testing were purchased in either pellet or liquid form. If pellets were used, then they were weighed (accuracy ±0.1g) and dissolved in RO water in a volumetric flask to a determined concentration, prior to addition to the main cleaning tank. If liquid cleaning formulations were used, they were measured and diluted to the required concentration prior to addition to the graduated cleaning tank (accuracy ±0.1 litre). Low concentrations were made up by serial dilutions and even distribution and mixing was ensured by pumping the cleaning solution through the recycle loop and mixing using an electric stirrer.
2. Cleaning solution temperatures were measured using Type K thermocouples (accuracy ±0.5°C) and the pressure drop across the glass test cell was measured using transducers. These were calibrated and regular intervals to ensure accurate operation.

Reproducibility of TOC

The results from a study of the reproducibility of the Dohrmann DC-180 are given in Table 4.4 for the determination of a prepared 100 ppm C standard. Overall, the stability of the system is good and variations in the determined concentrations can be explained by the difficulties in preparing and storing the inorganic standard.

Date	TIC (ppm C)	NPOC (ppm C)
6/2/94	87	58
7/2/94	97	49
8/2/94	96	66
9/2/94	107	65
10/2/94	98	57
11/2/94	88	58
Average	**96**	**59**
Standard Deviation	**8**	**6**

Table 4.4: Results from day-to-day reproducibility study for Dohrmann DC-180 Total Organic Carbon (TOC) Analyser.

CHAPTER 5: EXPERIMENTAL RESULTS AND DISCUSSION

5.1 INTRODUCTION

This chapter is divided into two main experimental sections: the first concerns a static cleaning study of potato starch deposit removal from stainless steel surfaces. The other, more detailed investigation involves the study of the cleaning of baked wheat starch deposits from stainless steel surfaces under controlled thermo-hydraulic conditions.

5.2 BACKGROUND

The relative efficiency of alternative cleaning procedures can only be assessed using a standard soil applied in a standard manner on a standard workpiece combined with a technique for measuring the amount of soil removed. In certain studies, the selected soil has contained a radioactive substance that is normally expensive and inconvenient to use but will give accurate results (Voss and Korpi [1972]).

An alternative method utilises a chemical dye that is cheaper and more convenient than radioisotopes but less accurate and reproducible. This method was adopted by Pohlman *et al.* [1972]; it involved coating a glass slide with black India ink and measuring the transparency of the slide using a photometer before and after cleaning in water. From these measurements the relative amount of dirt removed, i.e. the degree of cleaning (R_m), was calculated from the following equation:

$$R_m = \frac{M_1 - M_2}{M_1 - M_o} \tag{5.1}$$

where M_o is the mass of the uncoated glass plate, M_1 is the mass of the coated glass plate before cleaning, and M_2 is the mass of the coated glass plate after cleaning. The advantage of a gravimetric technique is that a cleaning efficiency can be obtained directly.

5.3 ORIGINS OF SONOCHEMICAL ACTIVITY

Power ultrasound exists in the range 18-100kHz. It enhances chemical reactivity in a liquid medium through the generation and destruction of cavitation bubbles (Walker [1985]). Like any sound wave, ultrasound is propagated by a series of compression and rarefaction waves induced in the molecules of the medium through which it passes. At sufficiently high power, the rarefaction cycle may exceed the attractive forces of the molecules of the liquid and cavitation bubbles will form. It is the collapse of these cavities over successive compression cycles which generates the energy for chemical and mechanical effects. So powerful is this inrush of liquid to fill the void that it will produce shear forces in the surrounding bulk liquid capable of breaking chemical bonds. In a heterogeneous solid/ liquid system, the collapse of the cavitation bubble will cause significant mechanical defects. Collapse near the surface produces an unsymmetrical inrush of fluid to fill the void with the result that a liquid jet is formed targeted at the surface. The effect is equivalent to high pressure jetting and is the reason why ultrasound is used for cleaning. The collapse is thought to generate very high local temperatures (around 5000°C) and pressures (in excess of 1000 atm) for very short periods of time (Walker [1985]).

In the rarefaction phase, the cavitation bubbles take up gas from the liquid and when the bubbles collapse during the compression phase this gas cannot completely redissolve; a certain residual volume remains and serves as a nucleus for a new cavitation bubble. According to Lord Raleigh [1917], the pressure pulse p during the collapse of a cavitation bubble obeys the proportionality

$$p \propto \left[\left(\frac{D_o}{D} \right)^3 - 1 \right]^{\frac{1}{2}} \tag{5.2}$$

where D_o is the maximum initial diameter of the bubble and D is the final, residual diameter.

The pressure p is a measure of the strength of cavitation; i.e. its cleaning effect. As the residual diameter decreases, therefore, the hardness of the pressure pulse increases. If the bath temperature is raised, the gas solubility and the residual diameter of the bubbles are decreased, and the increased hardness of the cavitation produces a greater cleaning effect.

Sonication of a liquid medium can therefore be thought of as generating high energy "hotspots" throughout the system.

5.4 PILOT ULTRASONIC EXPERIMENTS

As can be seen from the previous section, the effect of ultrasound is a large issue which is outside the scope of this investigation. Experiments were conducted to identify the key factors which influence the cleaning of modified potato starch from stainless steel in a static system. The major findings from these experiments are outlined in this chapter.

The procedure was aimed at producing a potato slurry which after baking would display both a high soil-soil and soil-substrate bond strength; thus representing a tough cleaning problem. This tenacious deposit was subsequently cleaned using a variety of cleaning agents. The effects of temperature and concentration on the cleaning ability of these agents was then investigated by studying the kinetic profile of the removal patterns observed.

5.4.1 Sample Preparation

In order to be able to compare kinetic runs and hence cleaning performance, a standard soiling process had to be established. The procedure used by Bird *et al.* [1993] was adopted to allow a comparison of previously obtained results in this area of study.

The source of carbohydrate in these experiments was obtained from a commercially modified potato starch called *Smash* containing 84 wt% starch (dry mass). This was purchased in an aggregate form and was ground into a fine powder for slurry preparation. The powder was air dried in an oven at 80°C for 30 minutes to remove any residual water.

A workable slurry was formed by adding 60.0 g of distilled water to 20.0 g of *Smash* and mixing well before allowing to stand for a minute.

5.4.2 Soiling Technique

Circular 50 mm diameter plates made of 316 stainless steel were used in these experiments. Each plate was indented with an identification symbol and the weight recorded to the nearest milligramme.

Approximately 4.00 g of slurry was applied to each plate using a small paint brush to obtain a smooth surface finish. The coated discs were then placed on a hot plate at a temperature of 330°C for a contact time of 4 minutes, producing a deposition mass of 493 g m^{-2}.The fouled plates were then allowed to cool slowly in a draught-free environment.

The deposit produced by this method possessed three distinctive features: In the centre of the deposit was an uncharred region referred to as the *inner potato crust.* This region was dome shaped and did not actually touch the plate surface. Surrounding this inner potato crust was a strongly attached charred region referred to as the *outer carbon ring.* Below the inner potato crust was a very thin film of charred carbohydrate referred to as the *inner carbon layer.*

5.4.3 Cleaning Rig

A 4.5 litre, 40 kHz, thermostatically controlled ultrasonic bath (*Decon Ltd.*) with a 100 Watt internal heater was employed to clean the fouled discs (see Figure 5.1). The required concentration of cleaning agent was added at ambient temperatures and then heated to the required temperature. (The addition of sodium hydroxide pellets caused a considerable increase in bath temperature due to the exothermic heat of solution.) Since the prior assumption would hold i.e. the cleaning action will be largely the mechanical removal of dirt due to the pressure pulses arising from the cavitation; the determining factor in this process is the amount of gas contained in the cleaning solution. For this reason, each time the bath was filled, the cleaning solution was degassed and left to stand overnight at constant temperature. Using this procedure, equilibrium of the gas content was achieved, thus ensuring the reproducibility of the test conditions in a series of experiments.

Once the bath had reached the required conditions, a stainless steel basket containing the fouled discs was gently lowered into the bath. The fouled discs were removed from the bath at regular intervals of time, rinsed with distilled water before air-drying at $50^{o}C$ in a fan-assisted oven until a constant dry mass of deposit was achieved.

For these pilot studies, two methods were employed to assess the cleaning performance from the surface of the hard surface:

1. The time taken for 95% removal of deposit from the surface,
2. The percentage deposit removed from the surface after 15 minutes.

The first criterion ensured that cleaning times were not distorted by small areas of tenacious deposits which would remain after the bulk of the material had been removed. The second criterion was adopted to provide a kinetic snapshot to enable cleaning agent concentration and temperature effects to be determined. For certain effective cleaners, a kinetic profile for removal was obtained over the initial 25 minute cleaning period. This was achieved by removing the test discs at set time intervals from the ultrasonic bath.

Throughout the cleaning process, the bath temperature was monitored using a mercury thermometer and the internal heater used appropriately to maintain a constant temperature. For the active cleaning agents with pH dependence, the pH was also recorded during the experiments. Visual observations were made during the whole cleaning process; paying particular attention to removal patterns for the different regions of the deposit.

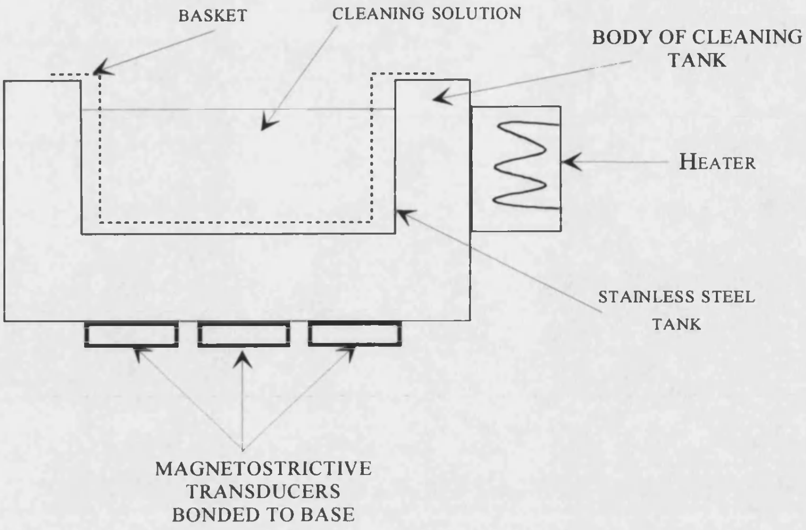


Figure 5.1 Schematic diagram of ultrasonic bath.

5.4.4 Experiments Performed

The following table summarises the experiments performed:

CLEANING AGENT	**CONCENTRATIONS INVESTIGATED (wt%)**	**TEMPERATURES (^{o}C) INVESTIGATED**
Distilled Water	-	25, 50, 55, 60
CONC. SWEEPS		
Sodium hydroxide	5, 8, 10, 12, 14, 16, 18, 20	60
Nitric Acid	1 ,2, 3	60
Micro	2, 4, 8	60
α-Amylase	0.02, 0.04, 0.06, 0.1	55
β-Glucanase	0.1, 0.2, 0.4	55
TEMP. SWEEPS		
Sodium hydroxide	14	46, 50, 53, 55, 58, 60, 62, 65
Nitric Acid	1	45, 50, 53, 55, 58, 60, 62, 65, 70
Micro	2, 4, 8	45, 50, 55, 57, 60, 65, 70, 80
α-Amylase	0.02	25, 40, 50, 63, 67
β-Glucanase	NA	NA

Table 5.1 Summary of experiments performed using the *Decon* ultrasonic bath.

5.4.5 Results

5.4.5.1 Sodium Hydroxide

The results showed that a concentration optimum exists for sodium hydroxide at 14 wt% (Figures 5.2 and 5.3). This concentration optimum was then used to perform a temperature sweep, the results of which suggest a temperature optimum exists at 60°C (Figure 5.4). Observations of the cleaning process indicated that swelling of inner potato crust deposit occurred before removal; indicating a hydrolysis reaction occurred between the caustic and the deposit. Further investigation into this observed mechanism using SEM techniques is described in Section 5.17.

5.4.5.2 Nitric Acid

Although no concentration optimum was evident from the range considered (Figure 5.5); the existence of an optimum temperature at 60°C was found for nitric acid (Figure 5.6). The nitric acid removal pattern was different to the caustic: small particles from the soil sample were removed and the soil became light in colour and the solution turned yellow indicating a hydrolysis reaction was occurring. Swelling of the inner potato crust was also visible.

5.4.5.3 *Micro*

The influence of increasing concentrations of *Micro* at 60°C had no significant effect on the overall cleaning efficiency for the time span considered (Figures 5.7-5.10). However, a clear temperature dependency trend is evident for the 2 wt% *Micro* over a 15 minute duration (Figure 5.11). It is apparent that temperature has minimal effect on removal over 55°C. A slight swelling of the inner potato crust was also seen during the cleaning process, probably due to one of the active ingredients of *Micro*: sodium hydroxide. The large increase in the degree of deposit removed is indicative of the inner potato crust lifting off from the stainless steel disc.

5.4.5.4 Alpha–Amylase

A concentration sweep was conducted for the enzyme BAN (Bacterial Amylase Novo) at a temperature of 55°C (Figures 5.12-5.15). The α-amylase showed a distinct relationship between the cleaning time and temperature over the range of concentrations considered (Figures 5.16-5.21). The induction time prior to removal increases with respect to a corresponding decrease in temperature; cleaning time removal was a stronger function of temperature than of concentration, over the parameter ranges considered.

5.4.5.5 Beta Glucanase

Using the enzyme β-glucanase, over the concentration range considered it was discovered that a concentration dependency on removal exists (Figure 5.22). However, an optimum concentration was not found for the range tested. The significant increase in deposit removal displayed after an initial induction period is attributable to the inner carbon ring lifting off from the test disc between 5 and 10 minutes (Figures 5.23-5.25).

5.4.6 Discussion

The initial experiments with distilled water alone closely resembled the observations found in the literature. It was found that after complete saturation, the inner potato crust swelled slowly and left the disc in small fibres. Work done by Zasypkin [1992] on the extrusion of potato starch at different temperatures also found a mechanism of swelling before appearing as 'microfibrils' when at the point of going into solution.

The optimum sodium hydroxide concentration of 14wt% found by these experiments coincided with the value obtained by previous work by Bird *et al.* [1993]. This value is significantly higher than the optimum sodium hydroxide concentration of 0.5 wt% for whey protein deposit removal (Bird [1993]).

The addition of the alkali contributed to the dissolution effects on the deposit. Although the caustic soda exhibits poor wetting properties, due to its high pH it was particularly effective at removing the burned-on inner and outer carbon ring. As mentioned earlier, ultrasound produces cavitation and powerful shock waves that rapidly help disperse the deposit in solution and this aided in the inner carbon ring becoming detached from the stainless steel disc.

The swelling effect exhibited by the soil had two effects on the detersive process. First it altered the nature of the soil surface making it more like a water surface.

Secondly, it allowed diffusion of bath components to the interior of the deposit, where they are adsorbed and taken out of action or may diffuse to the substrate-soil interface and get directly into the action of breaking the soil-substrate bonds: the cleaning efficiencies are low during the initial immersion stage but rapidly increase as the potato deposit lifts off the disc. This would provide an explanation for the marked swelling with increasing temperature. It is also worthy of note that significant reductions are achieved in the overall cleaning times when the bath temperature exceeds the gelatinization temperature of the potato starch (Figure 5.4).

The swelling phenomenon was noticed to be more pronounced in sodium hydroxide cleaning than when using nitric acid: When using sodium hydroxide, the inner potato crust started to swell initially and as a result cracks appeared in the inner potato crust where it joined the outer carbon ring. The remaining carbon then dissolved into the solution. However, nitric acid produced less initial swelling but removal of the potato crust was brought about by cracking and flaking action through the inner carbon layer until the exposed surface was bare metal.

These results agree with the work of Harper [1972] that sodium hydroxide interacts directly with carbohydrates whereas nitric acid attacks the surface without penetrating the soil and hence less swelling is observed. Harper implies that the main property of acid cleaning agents is to dissolve rather than to penetrate and emulsify the soil.

The influence of *Micro* concentration over the range investigated has no effect on the cleaning efficiency (Figure 5.10). This may be due to morphological changes occurring in the deposit inhibiting further removal at the higher concentrations investigated. A more detailed study using SEM techniques would be needed to justify this theory. However, a temperature dependency trend is evident for the range considered for the 2wt% *Micro* over 15 minute duration (Figure 5.11) and it is apparent that temperature has minimal effect on removal over 55°C (above the gelatinization temperature of the potato starch). Again, a microscopical investigation of the morphological changes in the deposit subjected to these conditions would provide a clearer explanation to the causes of this phenomena and also for the swelling of the inner potato crust observed.

BAN is an endo-amylase and it hydrolyses 1,4-α-glycosidic linkages in amylose and amylopectin at random, which results in a rapid reduction of the viscosity of gelatinized starch. The breakdown products are dextrins of different lengths and oligo-saccharides. According to the manufacturer of this enzyme, the upper limit of activity is 85°C, prior to denaturation. This value was not tested due to the limitations in the heating capacity of the ultrasonic bath. It is believed, however, that an optimum temperature of activity is likely for this enzyme according to the trend discovered in these experiments.

The action of β-glucanase on the starch deposit is to break the 1,6 linkages in the starch molecule constituting the amylopectin molecule. As stated earlier, the increase in concentration tends to decrease the removal time although an optimum was not determined from the range considered. It is also believed that an optimum temperature exists for soil removal using the β-glucanase, although this hypothesis was not tested experimentally.

It is proposed that the shape and size of the deposit particle may be important factors in governing the ease of removal from the hard surface. It has been reported (Corrieu [1981]), that particles less than 10 μm are often essentially unremovable from hard surfaces by normal detersive processes. In addition, lamellae tend to cling more tenaciously to a substrate because of their larger attachment and they also provide less traction for dislodging mechanical forces. However a microscopic verification of these theories was not performed for this soil.

A summary graph comparing the overall cleaning efficiencies for the cleaners investigated is depicted in Figure 5.27 for a temperature of 60°C and a residence time of 15 minutes.

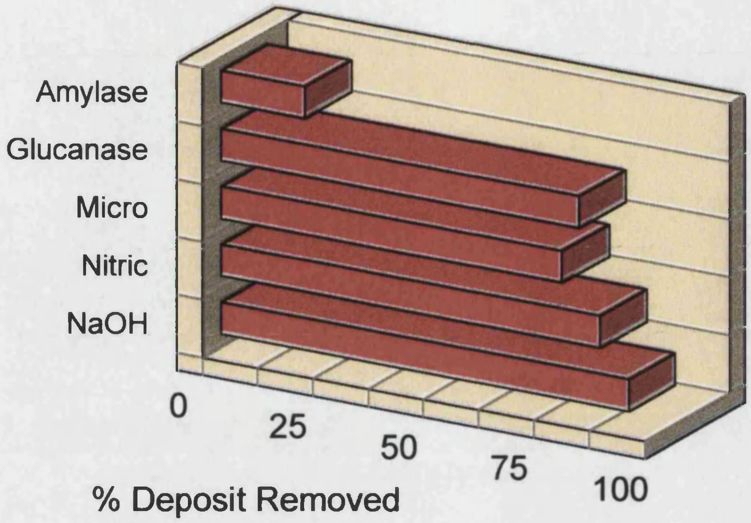


Figure 5.27 Summary of cleaning efficiencies for tested cleaners at 60°C for 15 minutes.

5.4.7 Conclusions

1. A concentration optimum was found when cleaning with sodium hydroxide at 14 wt%. This value agrees with previous work by Bird *et al.* [1993].

2. A temperature optimum exists above the gelatinization temperature of the potato starch, when cleaning with sodium hydroxide and this was found at 60°C.

3. A temperature optimum exists for nitric acid, but no concentration optimum was evident for the range considered.

4. The enzyme BAN (Bacterial Amylase Novo), an α-amylase, showed a strong dependence between the temperature and cleaning time, although no optimum temperature was found for the range considered.

5. For the enzyme β-glucanase, a concentration dependency exists for the removal rate of deposit over the range considered, although no optimum was found.

6. An increase in the concentration of the commercial cleaner (*Micro*) at 60°C did not affect the cleaning efficiency over the concentration range considered in these experiments.

7. The acid and alkaline cleaning agents act in different ways: the acid dissolves the substrate rather than penetrating and the sodium hydroxide emulsifies the soil.

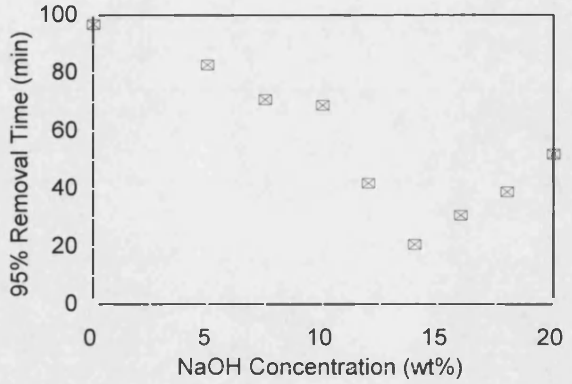


Figure 5.2: Effect of NaOH concentration upon potato starch removal time at 60°C.

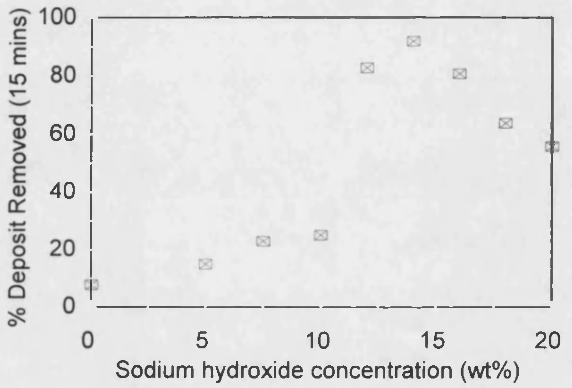


Figure 5.3: Effect of NaOH concentration upon potato starch removal time at 60°C after 15 minutes cleaning.

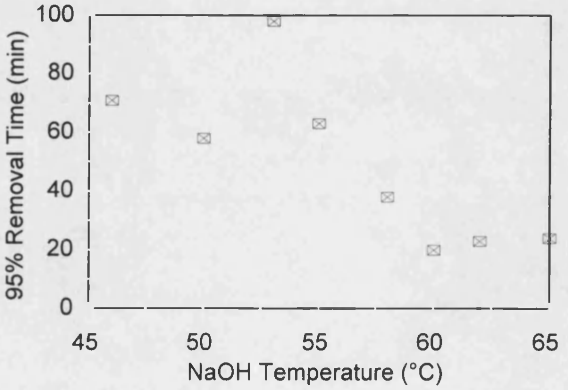


Figure 5.4: Effect of temperature upon potato starch removal time cleaned with 14 wt% NaOH.

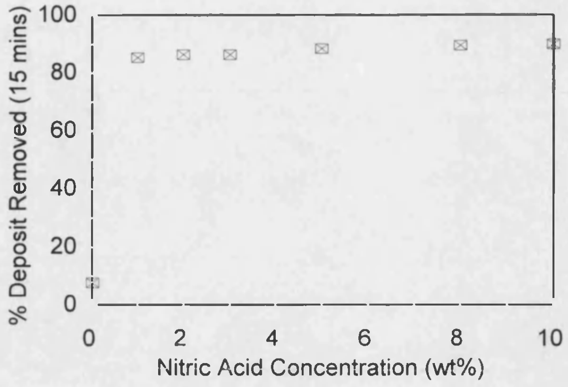


Figure 5.5: Effect of nitric acid concentration upon potato starch removal time at 60°C.

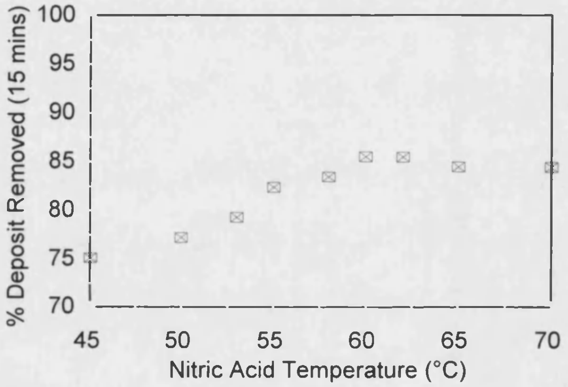


Figure 5.6: Effect of nitric acid temperature upon potato starch removal cleaned with 1 wt% nitric acid for 15 minutes.

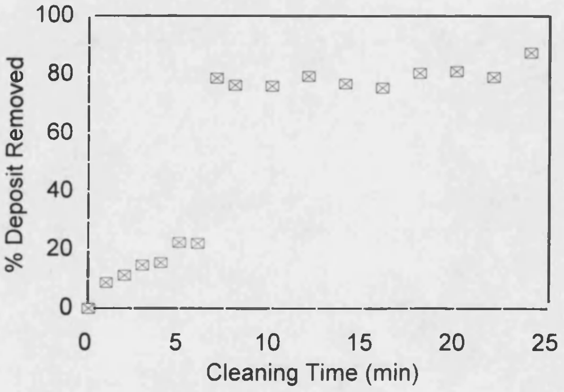


Figure 5.7: 2 wt% *Micro* kinetic sweep at 60°C.

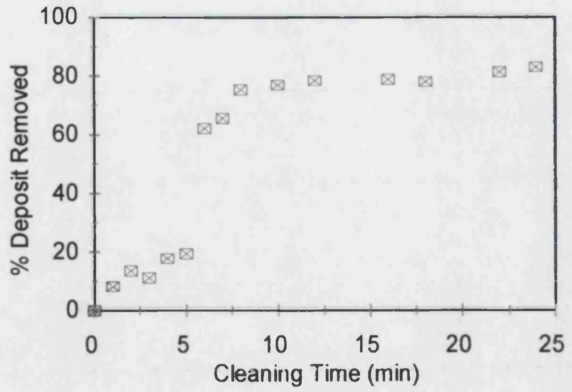


Figure 5.8: 4 wt% *Micro* kinetic sweep at 60°C.

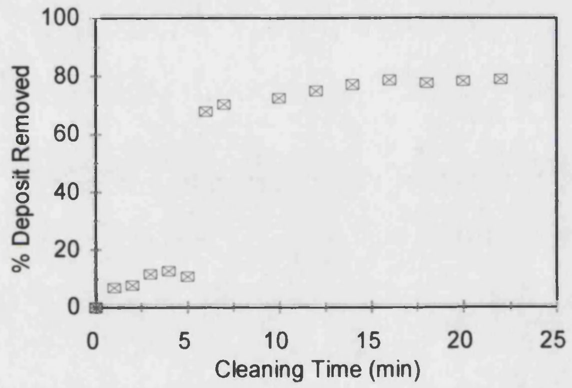


Figure 5.9: 8 wt% *Micro* kinetic sweep at 60°C.

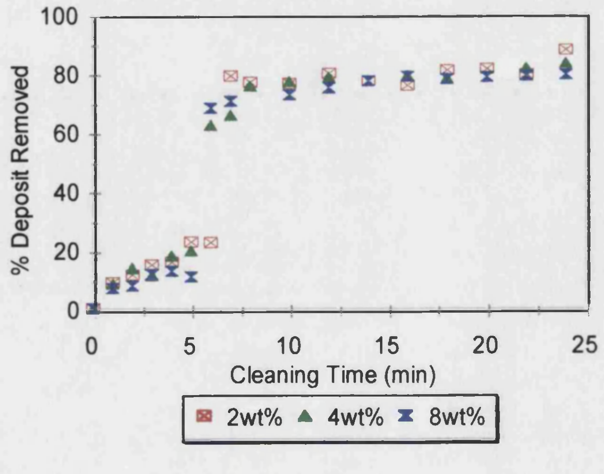


Figure 5.10: Overall *Micro* kinetic sweep at 60°C.

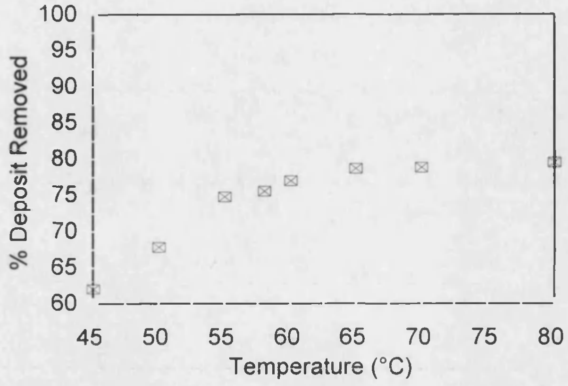


Figure 5.11: Temperature sweep for 2 wt% *Micro* (after 15minutes).

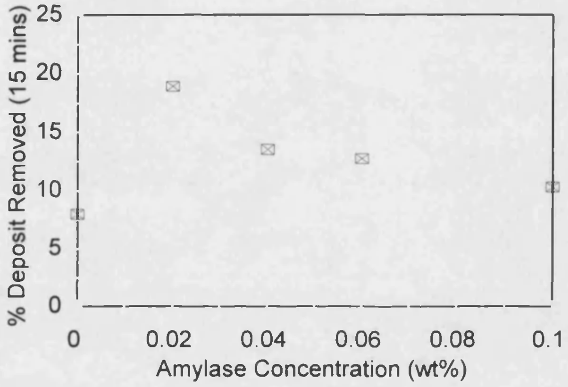


Figure 5.12: Concentration Sweep for α-amylase (after 15mins) at 55°C.

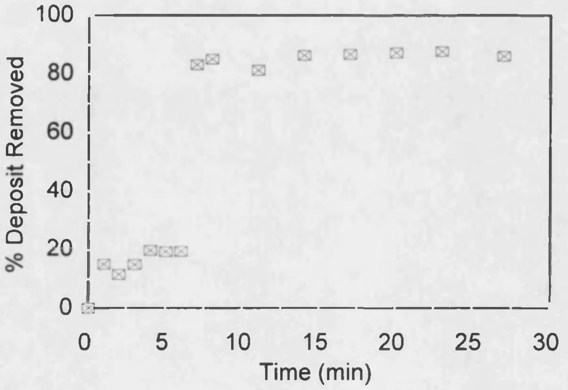


Figure 5.13: Kinetic profile for 0.04 wt% α-amylase at 55°C.

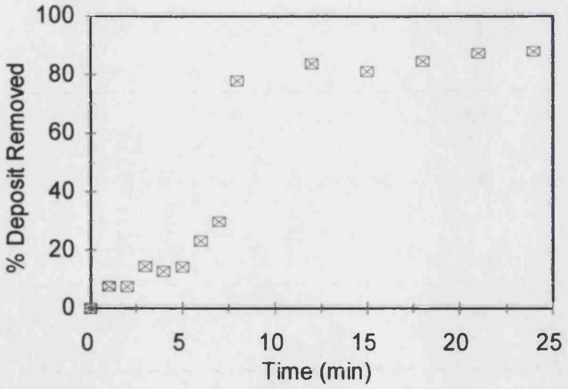


Figure 5.14: Kinetic profile for 0.06 wt% α-amylase at 55°C.

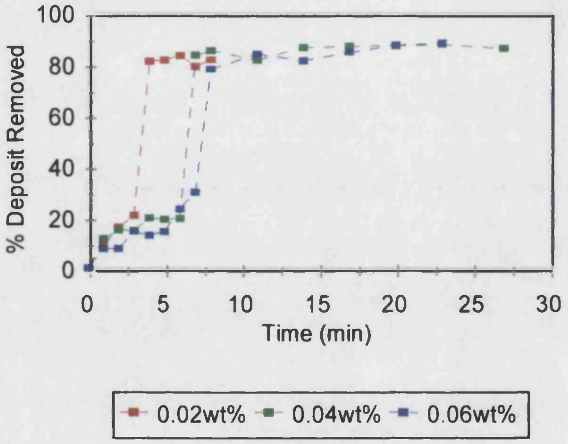


Figure 5.15: Overall kinetic profile for α-amylase at 55°C.

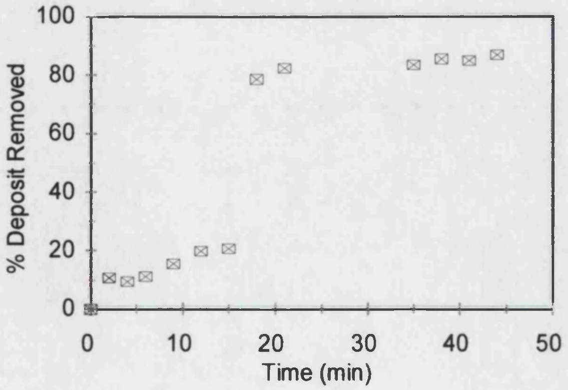


Figure 5.16: Cleaning profile for 0.02 wt% α-amylase, 25°C, pH=5

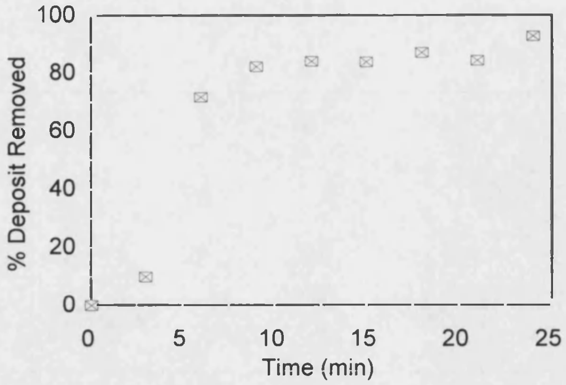


Figure 5.17: Cleaning profile for 0.02 wt% α-amylase, 40°C, pH=5

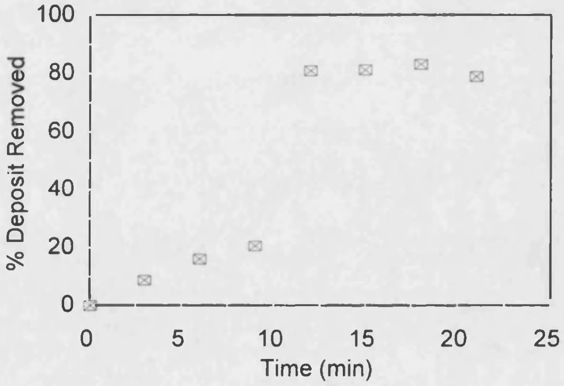


Figure 5.18: Cleaning profile for 0.02 wt% α-amylase, 50°C, pH=6.6

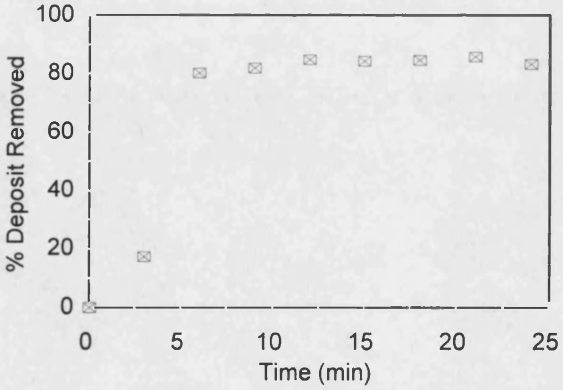


Figure 5.19: Cleaning profile for 0.02 wt% α-amylase, 63°C, pH=6.8

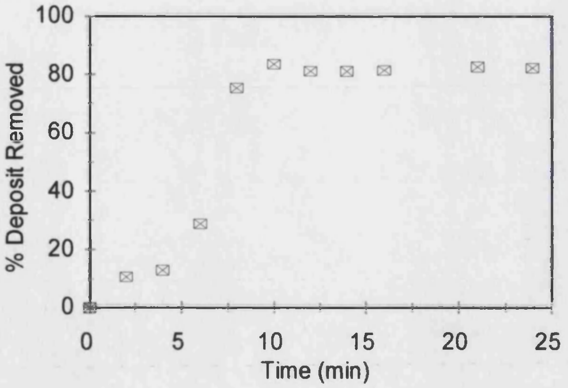


Figure 5.20: Cleaning profile for 0.02 wt% α-amylase, 67°C, pH=6.9

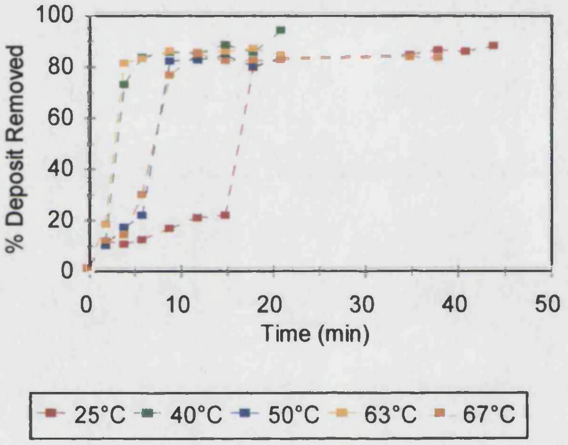


Figure 5.21: Temperature sweep profile for 0.02 wt% α-amylase.

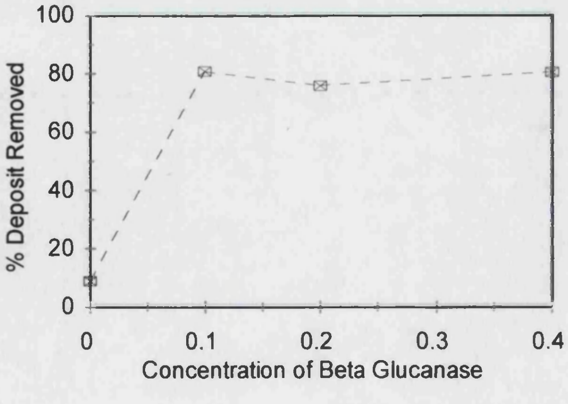


Figure 5.22: Concentration sweep for β-glucanase at 55°C (after 15 mins).

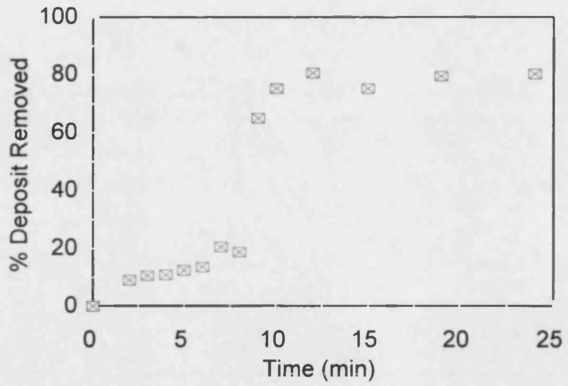


Figure 5.23: 0.1 wt% β-Glucanase at 55°C, pH=3.82

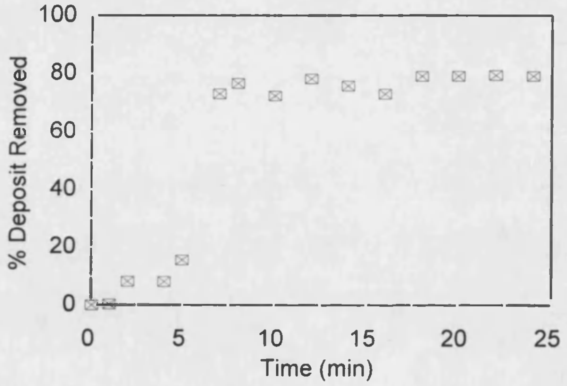


Figure 5.24: 0.2 wt% β-Glucanase at 55°C, pH=4.4

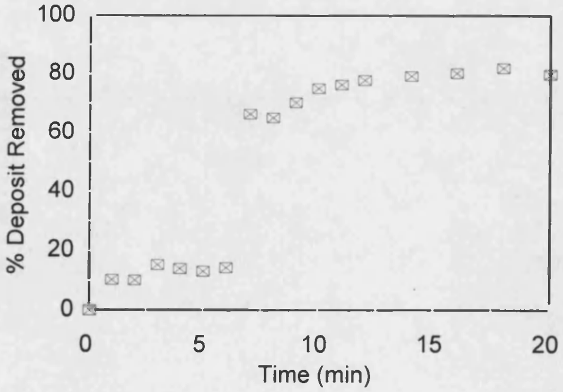


Figure 5.25: 0.4 wt% β-Glucanase at 55°C, pH=4.2

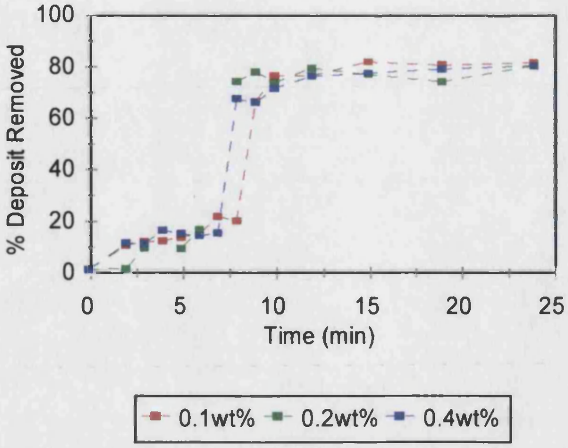


Figure 5.26: Overall kinetic profile for concentrations of β-glucanase investigated.

5.5 FLOW EXPERIMENTS: AN INTRODUCTION

The following sections describe the detailed experimentation programme aimed to provide fundamental information concerning the complex process of starch deposit removal in a flow system. The basis of these results provides the foundations for the development of the process modelling (Chapter 6), used to describe the mechanisms involved in this removal process.

5.6 EXPERIMENTAL PROGRAMME

The core results produced in this thesis for flow systems can be sub-divided into two sections: quantitative and qualitative evaluation of cleaning.

The former section makes up the majority of results presented in this thesis. These are presented in the form of removal curves as a function of time. The effect of individual parameters were investigated for each cleaner: cleaning solution temperature, shear-rate, composition and concentration.

Qualitative experimentation supplemented the data obtained by the above method for utilisation in the description of process modelling. It involved the observation of the cleaning process using a number of techniques including direct observation, video and still camera photography together with light and scanning electron microscopy.

5.7 QUANTITATIVE EVALUATION OF CLEANING

In this section, quantitative evaluation of the cleaning of wheat starch deposits from stainless steel test pieces is studied using a variety of aqueous cleaners. The removal patterns are examined as the degree of deposit removal (expressed as a percentage) versus a function of time. The influence of individual parameters; namely temperature, flow-rate and concentration of cleaning solution are investigated. The effects of increasing the deposit depth to 3 mm and ageing of foulant are also studied. A detailed study is then conducted for the most effective cleaner.

5.7.1 Typical Cleaning Curve

A typical cleaning curve is shown in Figure 5.28, the cleaning conditions were 50, 55, 60, 70, 80°C using 4 wt% $C_{9\text{-}11}E_6$ and a volumetric flow-rate of 4 l/min (linear velocity of 0.327 m/s). The y-axis represents the percentage starch deposit removed from the surface of the test-plate and the x-axis portrays the cleaning time (min).

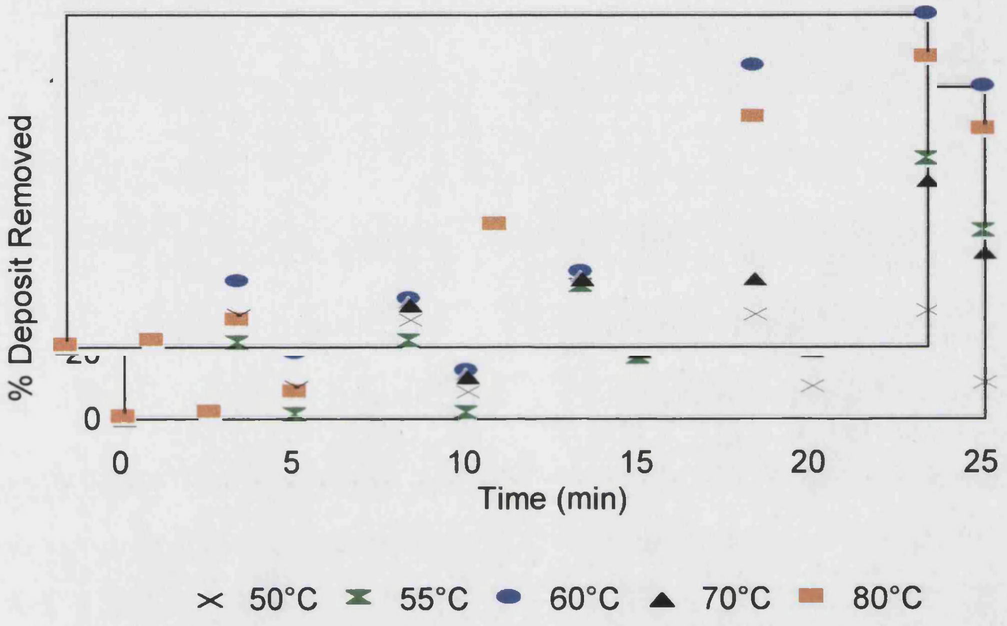


Figure 5.28: Kinetic investigation into soil removal for 4 wt% alcohol ethoxylate at varying cleaning temperatures at a velocity of 0.327 m/s (*Re* = 8605 at 60°C).

5.7.2 Cleaners Investigated

5.7.2.1 *Water*

Although rinsing has no chemical effect on cleaning, it is an elementary method of soil removal. Its effect on cleaning has been studied for a number of soil types (Paulsson [1989]), although no studies involving starch deposit removal by water have been found in the literature.

The removal is attributed solely to shear forces exerted on the deposit boundary layer when the rinsing water passes over it. This study investigates the influence of temperature and flow-rate of rinse water on the removal of the baked wheat starch deposit.

A comparison is also made on the effects of rinsing using two different water types: Reverse Osmosis (RO) and tap (hard) water.

5.7.2.2 *Sodium hydroxide (+EDTA/ Surfactant)*

Sodium hydroxide is a common alkali cleaner used for CIP applications in the food industry. It is cheap, has high alkalinity and rapid dissolving power and can also be used as a germicide. However, caustic soda is lacking in many desirable detergent properties and when used alone it is very corrosive to most metals other than stainless steel. Unless phosphate is present, caustic soda rapidly precipitates calcium and magnesium hardness from water. For these reasons, a comparison was made of the effectiveness of sodium hydroxide solutions and the effect of additives which may act synergistically with it: The chelating agent, EDTA (Ethylene Diamine Tetra-Acetic acid, $CH_2N(CH_2COOH_2))$ and a commercially available surfactant (*Synperonic* LF/CS 1000, *ICI Surfactants*), were studied in conjunction with a fixed sodium hydroxide concentration.

Due to its ability to combine with metals, EDTA is used industrially in specialist soaps for removing metallic contamination (Graβhoff [1989]).

Synperonic LF/CS 1000 is a low foaming biodegradable alkali-stable non-ionic surfactant. It is used in many heavy-duty cleaning operations, such as metal degreasing and bottle washing. It is a modified alcohol alkoxylate which has been designed for use in alkali cleaning formulations. It contains low foam wetting agents. These surfactants have chelating abilities which enable them to be effective in high hardness environments and enables them to sequester many metal ions including calcium, magnesium and iron. In addition to the performance properties in various applications, the materials display reasonable biodegradability in standard tests.

5.7.2.3 *Nitric Acid*

It was hypothesised that nitric acid; a strong but relatively non-corrosive mineral acid, may provide the needed detergency when combined with the temperature, concentration and fluid dynamic factors involved in CIP systems to adequately clean a tenaciously bound residual soil from a hard surface (White & Rabe [1969]).

Using nitric acid rather than the alkaline detergents now in general use may have several advantages: cost could be lowered significantly and nitric acid cleaning would enable use of a simple, inexpensive CIP system. In addition, nitric acid would be a very low cost detergent compared to commercial alkaline cleaners. Reduced cleaning time is also a potential advantage, allowing the operation of a food plant at a higher level of capacity.

A mineral acid detergent may be more effective in controlling hard water incrustations resulting from the precipitation of calcium and magnesium by alkaline cleaning. Nitric acid presents few disposal problems; the wash solution would quickly be diluted to a completely biodegradable waste product.

Nitric acid also possesses strong penetrating action which effects rapid washing away of soils. It also has good rinsability, which results in the acid and soil being rinsed away from the hard surface freely and rapidly after the desired cleaning has been accomplished. As a consequence of all these properties, it has been applied as a detergent in this investigation to increase fundamental knowledge on the mechanisms of starch soil removal from hard surfaces.

5.7.2.4 *Formulated Detergents (Micro-90, Metaflux Stark Cleaner)*

Experiments performed using formulated detergents are presented to allow performance comparisons with simple cleaners. Although details of the minor components in these complex chemical cocktails were not known it was possible to carry out concentration and temperature sweeps for these two cleaners.

The cleaning effects of a commercial basic (*Micro-90*, *Universal Products Ltd.*), and an acidic cleaner (*Metaflux Stark Cleaner, Precedent Industrial Products UK Ltd.*) were investigated: *Micro-90* is a formulated alkaline based cleaner whereas the *Metaflux Stark Cleaner* is an acidic-based cleaner (pH = 2.5) used in the food industry for dissolving organic and inorganic residues from hard surfaces.

5.7.2.5 *Enzymes (Thermophilic α-amylase, Diastase)*

The thermostable enzyme used was a bacterial α-amylase of food grade quality produced by a selected strain of *Bacillus amyloliquefaciens* (*subtilis*) (*Optiamyl,* supplied by *Genecor*). This is an endoenzyme which hydrolyses the α-1, 4 glucan bonds of starch (amylose as well as amylopectin), to form soluble dextrins.

In addition, the cleaning effect of a mixture of α-amylase and β-amylase (diastase from malt, *Merck Chemicals*) was studied for this deposit.

5.7.2.6 *Nonionic Surfactant*

The selected nonionic surfactant ($C_{9\text{-}11}E_6$) is a mixture of polyoxyethylene nonionic surfactants containing 13-23% C_9's, 36-48% C_{10}'s and 33-43% C_{11}'s with an average 6 moles of ethylene oxide (*ICI Surfactants, Wilton*). An anomaly of this surfactant molecule shape is that the hydrophilic portion is an elongated chain as opposed to the typical compact polar "head" associated with nonionic surfactants (Section 1.7.5).

5.8 RINSING EFFECT

The most fundamental form of cleaning is rinsing which has been studied in depth for various deposits (Paulsson [1989]), but little work has been reported for starch deposits (Linderer [1993]). Removal forces are created by the shear forces at the deposit boundary by the passing liquid. The values for surface shear stress were determined from a knowledge of the Reynolds number and are based on two equations for laminar (equation 5.3) and turbulent flow (equation 5.4) from Coulson & Richardson [1993]:

$$\tau = \frac{8\rho u^2}{\mathrm{Re}} \tag{5.3}$$

$$\tau = 0.0396\rho u^2\ \mathrm{Re}^{-0.25} \tag{5.4}$$

where τ is the surface shear stress, *Re* the Reynolds number, and ρ and u the cleaning solution density and velocity respectively.

The influences of rinse water temperature and flow-rate characteristics on the removal of a 2 mm depth wheat starch deposit have been investigated.

5.8.1 Effect of Rinse Water Temperature on Removal

The rinsing of a 2 mm wheat starch deposit, using reverse osmosis (RO) water, has been studied at temperatures of 20, 50, 60, 70 and 80°C at a flow-rate of 4 l/min, a velocity of 0.341 m s^{-1} and a Reynolds number range of 4074-9875 over a 25 minute cleaning time. Figure 5.29 depicts the temperature sweeps for two concurrent runs under these conditions.

A similar plot has been constructed for comparison under these conditions using hard tap water (Figure 5.30). In both cases, a degree of swelling was apparent in the soil deposit when subjected to the rinsing indicating a diffusion to occur from the bulk liquid to the soil interface (Section 1.4). Further implications of this phenomenon are discussed in Chapter 6.

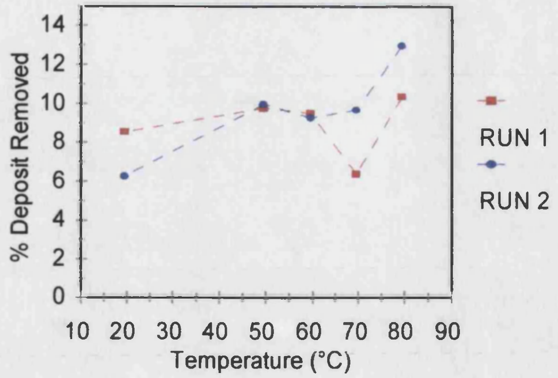


Figure 5.29: Temperature sweep for 2 mm wheat starch deposit removal over 25 minute cleaning time using RO water, velocity of 0.341 m/s (Re = 4074-9875).

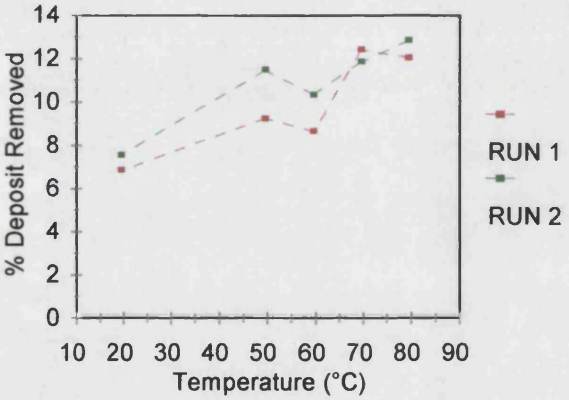


Figure 5.30: Temperature sweep for 2 mm wheat starch deposit removal over 25 minute cleaning time using tap (hard) water, velocity of 0.341 m/s (Re = 4074-9875).

5.8.1.1 *Discussion of results*

It is clear from Figure 5.29 that increasing the RO water temperature had minimal effect on deposit removal under the flow conditions studied. Temperatures in excess of 50°C for rinsing produced ~10% cleaning efficiency over this time-scale. This promotes the fact that cleaning starch deposits is a tough cleaning problem.

A similar trend was observed for the cleaning using tap water under similar temperature and flow conditions (Figure 5.30). There is little discernible difference between the points rinsed with RO water (20 μS/cm) or hard water (600 μS/cm). This suggests that the effects of hard tap water additives were minimal on the cleaning process. However, the soft RO water was selected for experimentation since it minimised additive influences and reduced the precipitation of calcium and magnesium salts in the presence of caustic based cleaners.

5.8.2 Effect of Rinse Water Velocity on Removal

The effect of rinse water velocity on wheat starch deposit removal has been characterised in Figure 5.31. A wide range of velocities have been studied (0.08 to 0.49 m s^{-1}) at 50°C; primarily in the turbulent flow regime. Flow-rates of 1, 2, 4, 6 l/min with Reynolds numbers of 1845, 3690, 7380 and 11070 respectively are presented. Two experimental runs were carried out at each flow-regime condition over a 25 minute cleaning period for a 2 mm depth baked wheat starch deposit.

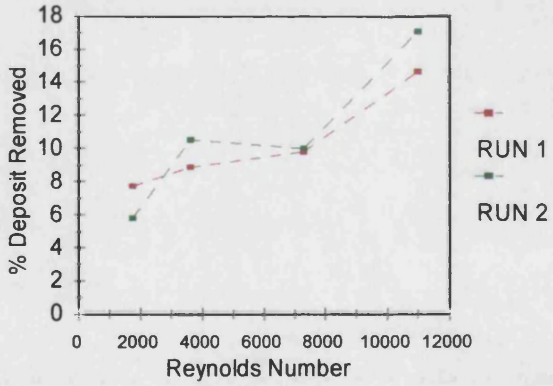


Figure 5.31: Effect of rinse water Reynolds number upon a 2 mm wheat starch deposit removal over 25 minute cleaning time using RO water at 50°C.

5.8.2.1 *Discussion of results*

For the range of flowrates considered at this temperature, increasing the velocity and hence the Reynolds number from laminar, through transitional to turbulent flow resulted in an increase in the removal achieved using RO water. This appears to be a linear relationship and it seems plausible to expect cleaning efficiency of rinsing to be directly proportional to the velocity, and hence the Reynolds number without any chemical effect. However, due to the tenacious nature of the deposit considered, the overall removal of deposit was marginal over the 25 minute duration.

Schlussler [1970] suggested that a critical Reynolds number had to be exceeded before cleaning could commence. The results obtained contrast with this view, indicating some removal is apparent even under the laminar flow conditions investigated.

5.9 SODIUM HYDROXIDE

5.9.1 Effect of sodium hydroxide concentration upon wheat starch deposit removal

Wheat starch deposit removal was studied for sodium hydroxide concentrations of 0.0, 0.1, 0.25, 0.5, 1, 3, 5, 10 wt% at 50°C and a Re = 7380 (velocity = 0.33 m/s) after a 25 minute cleaning duration. The results are presented in Figure 5.32 and 5.33.

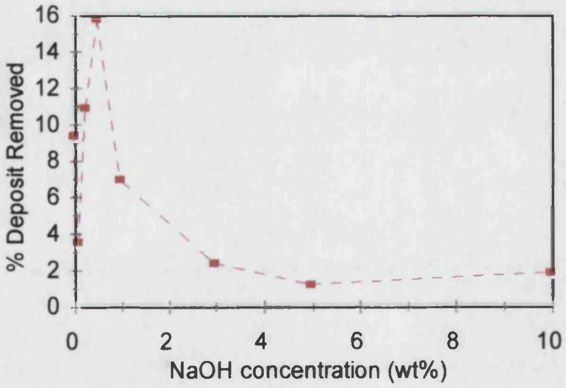


Figure 5.32: Overall sodium hydroxide concentration sweep effect on overall cleaning efficiency upon a 2 mm wheat starch deposit removal over a 25 minute duration, cleaned at 50°C and 0.33 m/s (Re = 7380), showing the existence of an optimum at 0.5 wt%.

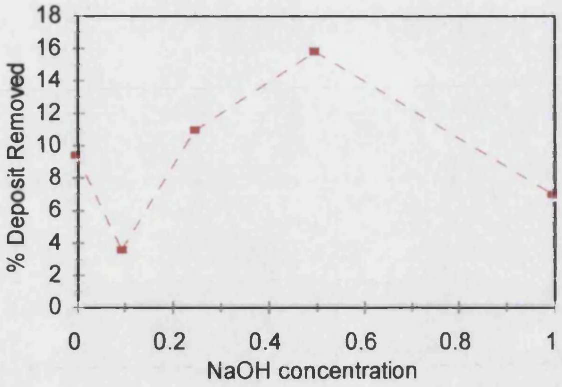


Figure 5.33: Low end concentration sweep of sodium hydroxide and its effect on the overall cleaning efficiency upon a 2 mm wheat starch deposit removal over a 25 minute duration, cleaned at 50°C and 0.33 m/s (Re = 7380), showing the existence of an optimum at 0.5 wt%.

5.9.1.1 *Discussion of results*

The overall cleaning effectiveness of sodium hydroxide was poor; the test-plate surface remained heavily fouled after the 25 minutes of cleaning. Only a small increase in removal efficiency (5%) was achieved by employing 0.5 wt% sodium hydroxide compared to the case when no cleaning chemical was used (pure RO water).

When 0.1 wt% sodium hydroxide was used, a decrease in overall cleaning efficiency was witnessed compared to pure RO water (Figure 5.33). However, a further increase in the cleaning solution concentration to 0.25 wt% led to a cleaning efficiency similar to that of water. At a sodium hydroxide concentration to 0.5 wt%, a cleaning optimum was displayed resulting in a maximum of 16% deposit removal after 25 minutes. However, further concentration increases up to 10 wt% NaOH tended to cause a dramatic change in the cleaning efficiency. Instead of a greater efficiency with increasing concentration there was a decrease in the cleaning efficiency. This suggests that excess sodium hydroxide changes the deposit to a form which is difficult to remove by fluid shear.

The existence of a cleaning solution optimum (0.5 wt%) has also been reported for caustic soda in the cleaning of whey protein deposit from hard surfaces by Bird [1993]. The morphological changes that the deposit undergoes when subjected to strong caustic soda conditions have been examined using SEM techniques, which can be used to explain the optimum observed and the apparent inhibition effects observed at low concentrations (Section 5.17).

5.9.2 Effect of sodium hydroxide temperature upon wheat starch deposit removal

To investigate the effect of temperature, both cleaning solution flow-rate and concentration were held constant. Experiments are presented at the optimum cleaning solution concentration of 0.5 wt%, under fully developed turbulent flow at a velocity of 0.33 m/s (Re = 7380 @50°C) over a 25 minute duration. Due to viscosity changes with temperature, the Reynolds number is greatly affected, and temperatures between 40-70°C were studied. The results are presented in Figure 5.34.

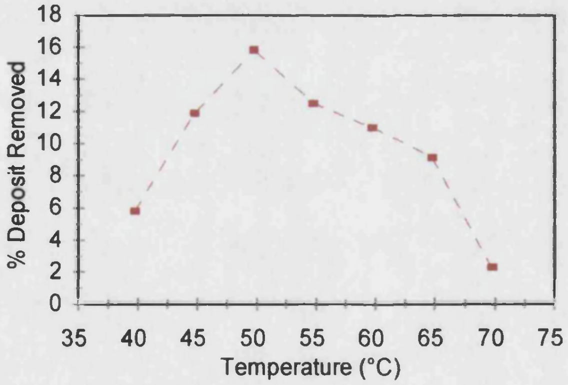


Figure 5.34: Effect of temperature upon the removal of wheat starch deposit cleaned by an optimum 0.5 wt% NaOH concentration and 0.33 m/s.

5.9.2.1 *Discussion of results*

An interesting temperature dependency relationship was discovered using sodium hydroxide at these flow conditions. An increase in temperature from 40 to 50°C caused an expected increase in overall deposit removal. However, further increases in in temperature resulted in a corresponding decrease in overall cleaning. An optimum temperature for removal thus exists at 50°C under these thermo-hydraulic conditions. An explanation for the unexpected decrease in cleaning efficiency may be attributed to a change in deposit morphology and will be discussed in more detail in Section 5.17.

5.9.3 Effect of fluid velocity upon wheat starch removal using sodium hydroxide

The effect of 0.5 wt% sodium hydroxide at 50°C and a velocity range of 0.08-0.49 m/s (Re = 1845 - 11070), on wheat starch deposit removal was investigated. The results have been presented in Figure 5.35.

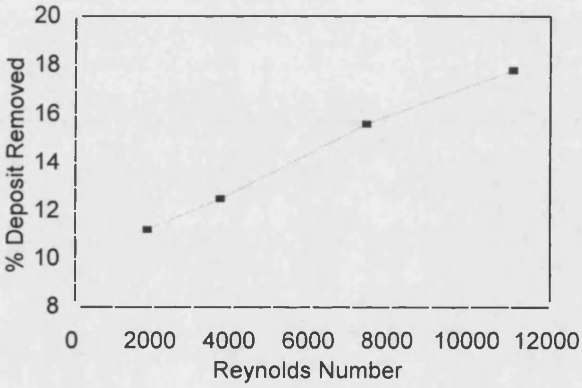


Figure 5.35: Effect of fluid velocity (0.08-0.49 m/s) upon the removal of wheat starch deposit cleaned by 0.5 wt% NaOH at 50°C after 25 minute duration.

5.9.3.1 *Discussion of results*

Increasing the sodium hydroxide velocity resulted in an increase in the overall cleaning efficiency observed over the 25 minute duration. As the velocity increased, the flow regime changed from laminar to turbulent flow and the cleanliness increased. This result agrees with the work of Jennings, McKillop & Luick [1957], who found that turbulence was more important than temperature in circulation cleaning of milk soils. However, a significant proportion of the deposit remained attached to the surface of the test-plate after each of the cleaning runs, indicating the strong soil-substrate and soil-soil bonds cannot be broken by shear forces exerted by the sodium hydroxide solution under these conditions. This is due to the soil system used in this experimentation represents a very severe fouling situation, most plant-cleaning problems will be less severe.

5.9.4 Determining a Cleaning Kinetic Profile using TOC analysis

A study of the effluent stream samples implementing TOC techniques enabled the determination of a cleaning kinetic profile. Sodium hydroxide was studied at the isolated optimal temperature and concentration conditions (50°C and 0.5 wt%), for a flow-rate of 4 l/min, Re = 7380. The results are presented in Figure 5.36.

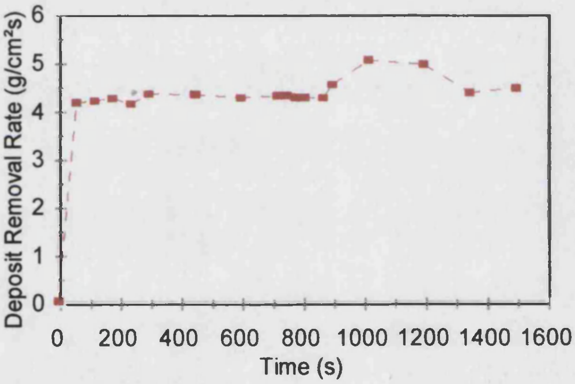


Figure 5.36: Effect of 0.5 wt% NaOH at 50°C upon the rate of removal of a 2mm depth baked wheat starch deposit using TOC analysis; Re = 7380.

5.9.4.1 *Discussion of results*

The cleaning curve depicted indicates that the removal pattern is non-uniform. The visualisation experiments support these findings (Section 5.17): the deposit swells and breaks up into lumps which are then removed by fluid shear. However, a clean surface is not achieved using sodium hydroxide under the thermo-hydraulic conditions and time-span considered. This may be a reflection on the tenacious nature of the deposit and also the poor wetting properties of the sodium hydroxide.

Implications of the removal mechanisms are further discussed in Chapter 6 of this thesis.

5.9.5 Effect of EDTA concentration upon wheat starch deposit removal at 0.5 wt% NaOH

An industrially relevant concentration of EDTA (2 g/l) was added to the sodium hydroxide cleaning solution. Wheat starch deposit removal was studied for sodium hydroxide concentrations of 0.25, 0.5, 1, 3, 5 wt% containing 2 g/l of EDTA at 50°C and a Re = 7380 (velocity = 0.33 m/s) after a 25 minute cleaning duration. The results are presented in Figure 5.37.

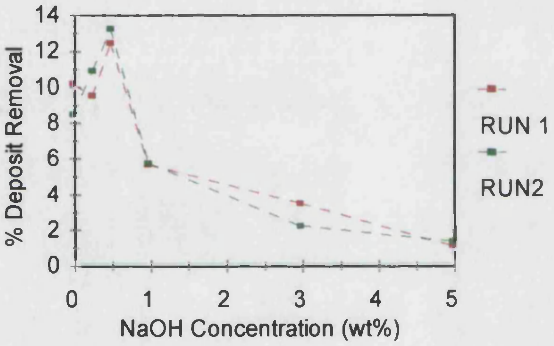


Figure 5.37: Concentration sweep for NaOH + 2 g/l of EDTA and its effect upon removal of a baked 2 mm wheat starch deposit over a 25 minute duration, cleaned at 50°C and 0.33 m/s (Re = 7380), showing the existence of an optimum at 0.5 wt%.

5.9.5.1 *Discussion of results*

The addition of the chelating agent EDTA to the 0.5 wt% sodium hydroxide appeared to have minimal effect on the overall cleaning effectiveness; the test-plate surface still remained heavily fouled after the 25 minute cleaning duration. This implies the EDTA was not effective at attaching to the starch deposit as is the case with proteinaceous materials (Graβhoff [1989]).

Although the cleaning efficiency graph shape mimics that using sodium hydroxide alone (Figure 5.32), there appears to be a slight decrease in overall cleaning efficiency using EDTA (-2%). This may be as a result of EDTA inhibiting the penetration of sodium hydroxide into the deposit. However, the existence of a cleaning optimum at 0.5 wt% sodium hydroxide still persists even in the presence of the EDTA under these conditions.

5.9.6 Effect of *Synperonic LF/CS 1000* concentration and temperature upon wheat starch deposit removal using 0.5 wt% NaOH

Wheat starch deposit removal was studied for a sodium hydroxide concentration of 0.5 wt% containing 0.01, 0.05, 0.2, 0.4, 0.8 *Synperonic LF/CS 1000* at 50, 60, 70°C and a Re = 7380-9875 (velocity = 0.33 m/s) with a 25 minute cleaning duration. The results are presented in Figure 5.38.

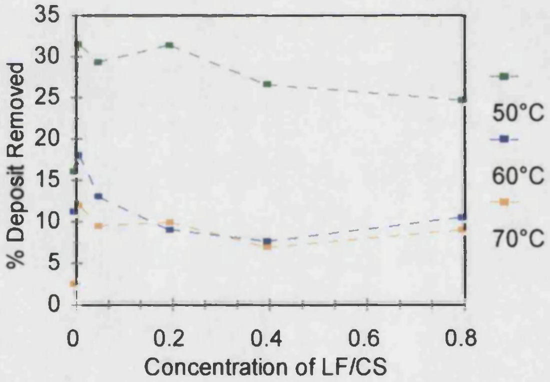


Figure 5.38: Cleaning effect of *Synperonic LF/CS 1000* at varying concentrations + 0.5 wt% NaOH at 50, 60, 70°C upon baked 2 mm wheat starch samples.

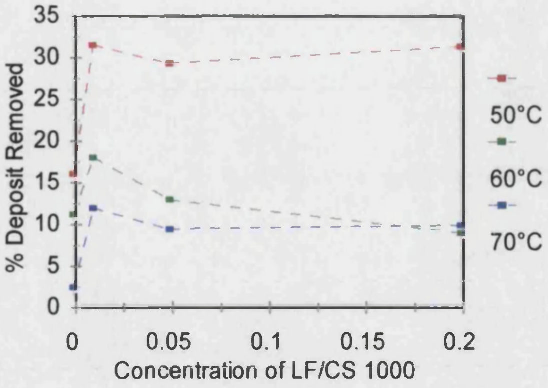


Figure 5.39: Cleaning effect of *Synperonic LF/CS 1000* at low-end concentrations + 0.5 wt% NaOH at 50, 60, 70°C upon baked 2 mm wheat starch samples.

5.9.6.1 *Discussion of results*

The addition of *Synperonic LF/CS 1000* to the 0.5 wt% NaOH solution resulted in an overall improvement in cleaning efficiency (up to 100%). The alkali alkoxylate therefore acts synergistically with the sodium hydroxide by improving the wetting properties of the solution to enable better soil penetration and removal of deposit from the hard surface.

A cleaning concentration optimum was also isolated with the use of the *Synperonic LF/CS 1000* at 0.01 wt% resulting in an overall removal of 31% at 50°C over the 25 minute duration (Figure 5.39). Further increases in concentration had an inhibitory effect on cleaning: 0.8 wt% *Synperonic* (80 times the optimum concentration), resulted in 24% overall removal at the same temperature.

In line with these findings, an optimum cleaning temperature was also isolated at 50°C. This optimum is above the cloud point temperature for this surfactant (45°C).

5.10. NITRIC ACID

5.10.1 Effect of nitric acid concentration upon wheat starch deposit removal

Wheat starch deposit removal was studied for nitric acid concentrations of 0.5, 1, 2, 5, 7 wt% at 70°C and a velocity = 0.33 m/s (Re = 9875) with a 25 minute cleaning duration. The results are presented in Figure 5.40.

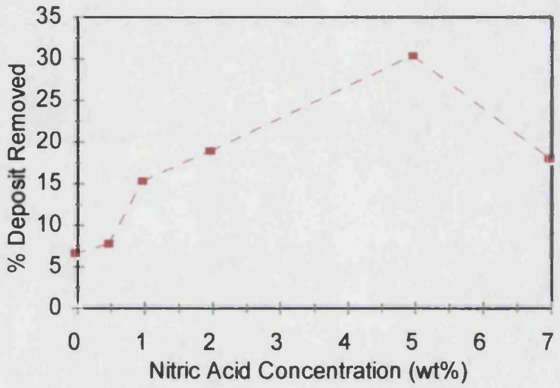


Figure 5.40: Overall nitric acid cleaning concentration sweep upon a 2 mm wheat starch deposit over a 25 minute duration, cleaned at 70°C and 0.33 m/s (Re = 9875), showing the existence of a concentration optimum at 5 wt%.

5.10.1.2 *Discussion of results*

As the nitric acid concentration was increased, the overall cleaning efficiency increased to a maximum of 30% removal at 5 wt% over the 25 minute duration and a temperature of 70°C. Further increases in nitric acid concentration resulted in a decrease in the overall removal of deposit from the stainless steel test-plates. Hence, an optimum was displayed under these thermo-hydraulic conditions.

This cleaning concentration optimum value of 5 wt% resulted in a significantly higher degree of deposit removal than with the use of sodium hydroxide yielding an optimum removal of 16% at 0.5 wt%. This implies that the nitric acid is a more effective cleaner under its optimum operating conditions than caustic soda.

It is possible that the higher nitric acid levels reduces the ability of the detergent to penetrate or wet the soil by increasing the interfacial tension. It has been found from the literature that the position of the optimum is a function of the soil type, its quantity, age, moisture and its strength of adhesion to a surface (Goederen *et al.* [1989]). Again, a study of the morphological structural changes occurring in the deposit using SEM techniques (Section 5.11), will help account for some of these phenomena.

5.10.2 Effect of nitric acid temperature upon wheat starch removal

To investigate the effect of temperature, both cleaning solution flow-rate and concentration were held constant. Experiments are presented at the optimum cleaning solution concentration of 5 wt% and also at 1 wt% for a comparison, under fully developed turbulent flow at a velocity of 0.33 m/s (Re = 7380 @50°C) for a 25 minute duration. Due to viscosity changes with temperature, the Reynolds number was greatly affected. Temperatures between 40-70°C were studied and the results are presented in Figure 5.41.

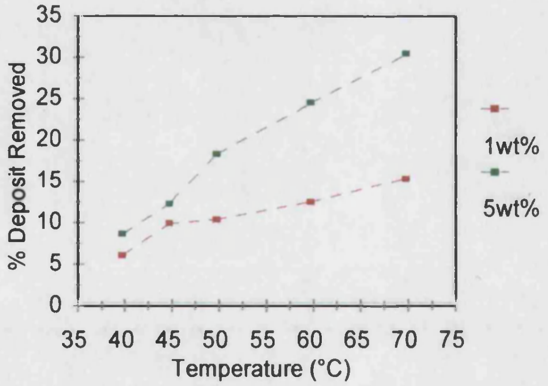


Figure 5.41: Comparison of temperature effects on wheat starch deposit removal over a 25 minute duration using 1 wt% and 5 wt% nitric acid at a velocity of 0.33 m/s.

5.10.2.1 *Discussion of results*

As Figure 5.41 clearly depicts the temperature is an extremely significant parameter in the cleaning operation when using nitric acid. It is likely that increasing the temperature of the nitric acid:

(a) decreases the strength of bonds between the soil and the surface

(b) decreases viscosity and increases turbulent action

(c) increases the solubility of the soluble materials

(d) increases chemical reaction rates.

For the starch deposit considered within the cleaning temperature ranges considered from 40° to 70°C, an increase of 10°C caused an approximate doubling of the cleaning operation observed for the 5 wt% nitric acid cleaner. However, no temperature optimum was isolated under these conditions for either cleaner concentration. It is likely though, that a maximum temperature does exist above which cleaning efficiency will decrease. This would be due to high temperatures causing the protein matrix binding the deposit more tightly to the surface and decreasing the cleaning efficiency. However, this theory cannot be tested experimentally due to operating restrictions of the rig.

5.10.3 Effect of fluid velocity upon wheat starch removal using nitric acid

The effect of 1 wt% nitric acid at 70°C and a velocity range of 0.08-0.49 m/s (Re = 1845 - 11070), on wheat starch deposit removal was investigated (Figure 5.42).

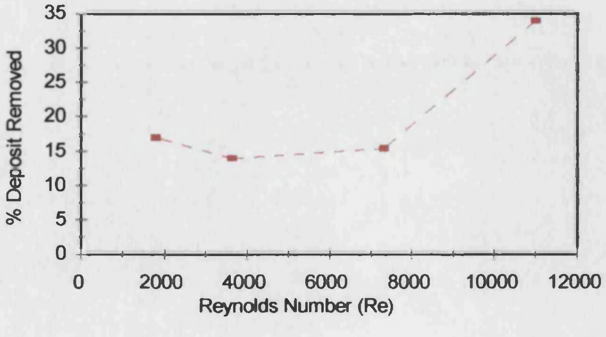


Figure 5.42: Effect of fluid velocity (0.08-0.49 m/s) upon the removal of wheat starch deposit cleaned by 1 wt% nitric acid at 70°C after a 25 minute cleaning duration.

5.10.3.1 *Discussion of results*

The effect of an increasing the flowrate (and hence the fluid velocity) from 1 l/min to 6 l/min at 70°C and 1 wt% nitric acid resulted in an increase in the overall cleaning efficiency observed for a cleaning time of 25 minutes. Interestingly, a laminar flowrate of 1 l/min (Re = 1845) had a similar overall cleaning effectiveness (16 %) to fully developed turbulent flow 4 l/min (Re = 7380). This suggests a critical shear stress is needed before soil/substrate bonds can be broken and the surface cleaned.

A significant proportion of the deposit remained attached to the surface of the test-plate after each of the cleaning runs (74%), indicating that the strong soil-substrate and soil-soil bonds cannot be broken by shear forces exerted by nitric solution under these conditions. This is due to the soil system used in this experimentation representing a very severe fouling situation, most plant-cleaning problems would be less severe.

5.11 FORMULATED DETERGENTS

5.11.1 *Effect of Micro-90 concentration upon wheat starch deposit removal*

Experiments were carried out at concentrations of 2, 3, 5, 7.5 and 10 wt% of *Micro-90*. A temperature of 70°C and Reynolds number = 9875 (velocity = 0.33 m/s) were employed. Results are presented in Figure 5.43.

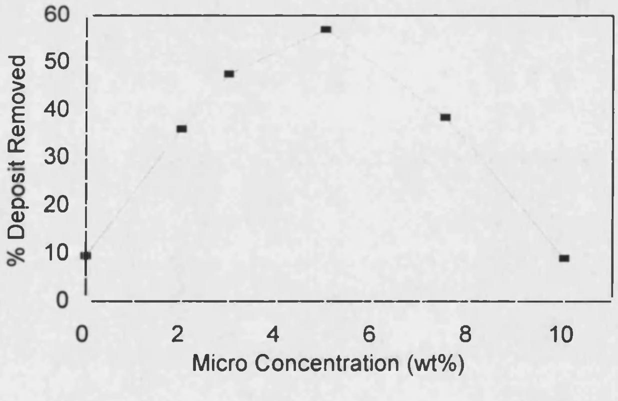


Figure 5.43: Overall *Micro-90* cleaning concentration sweep upon a 2 mm wheat starch deposit over a 25 minute duration, cleaned at 70°C and 0.33 m/s (Re = 9875), showing the existence of a concentration optimum at 5 wt%.

5.11.1.1 *Discussion of results*

Figure 5.43 clearly depicts an optimum detergent concentration for the *Micro-90* under these conditions at 5 wt% resulting in a deposit removal of 57%. This cleaning efficiency is significantly higher than that achieved using sodium hydroxide alone. This may be attributed to the enhanced properties of this alkaline cleaning cocktail by the action of non-ionic surfactants which promote good wetting and suspension properties. However, detailed formulation analysis of the cleaning constituents is not available from the manufacturer and the subsequent influences of each component on cleaning cannot therefore be easily investigated. An investigation into the influence of a nonionic surfactant on cleaning the wheat starch deposit is described in Section 5.13.

5.11.2 Effect of *Micro-90* temperature upon wheat starch deposit removal

The effect of temperatures between 40-70°C were studied using the optimum concentration of *Micro-90* isolated from the previous section. The experiments presented were performed using 5 wt% *Micro-90* at 40, 45, 50, 55, 60, 65 and 70°C at fluid velocity 0.33 m/s over a 25 minute cleaning duration (Figure 5.44).

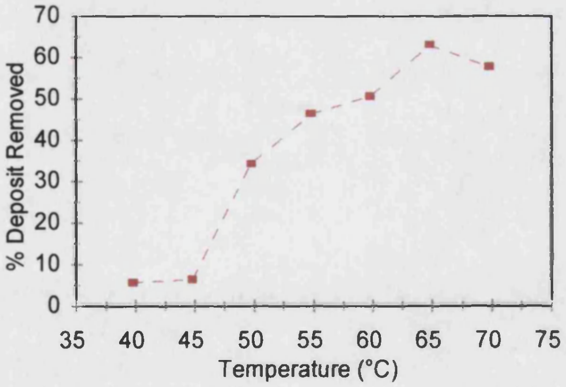


Figure 5.44: Overall *Micro-90* cleaning temperature sweep upon a 2 mm wheat starch deposit removal over a 25 minute duration using 5 wt% *Micro-90* at a velocity of 0.33 m/s.

5.11.2.1 *Discussion of results*

When the temperature was increased from 40 to 45°C there was no significant change in the overall cleaning efficiency. However, when the temperature was further increased to 50°C there was a dramatic change in the cleaning performance over this duration. The use of increasing temperatures produced further improvement up to 70°C. Although no cleaning temperature optimum is clear over the range studied, it is apparent that cleaning using *Micro-90* is very temperature dependant i.e. increasing efficiency with corresponding temperature rise.

5.11.3 Effect of *Metaflux Stark* cleaner concentration upon wheat starch deposit removal

Experiments were performed at concentrations of 0.1, 0.25, 0.5, 1, 2, 4, and 6 wt% of *Metaflux Stark* cleaner. A temperature of 50°C and Reynolds number = 7380, (velocity = 0.33 m/s) was employed. Results are presented in Figure 5.45.

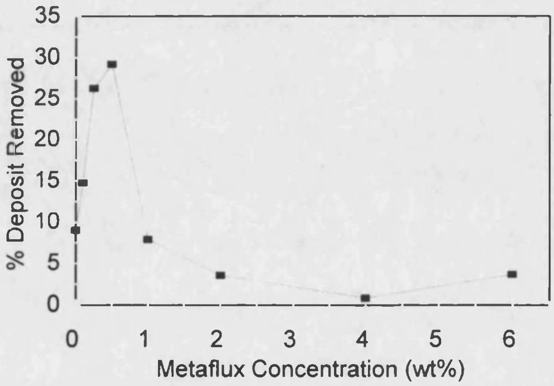


Figure 5.45: Overall *Metaflux Stark* concentration sweep for the cleaning of a 2 mm wheat starch deposit over a 25 minute duration at 50°C, 0.33 m/s (Re = 7380), showing the existence of a concentration optimum at 0.5 wt%.

5.11.3.1 *Discussion of results*

An optimum detergent concentration for the acidic *Metaflux Stark* cleaner was observed under these conditions at 0.5 wt% resulting in a deposit removal of 29%. This cleaning efficiency value was significantly higher than that obtained using nitric acid at this concentration alone under similar thermohydraulic conditions (Section 5.10.1). The enhanced properties of this acidic cleaning cocktail may be attributed to the synergistic action of the nonionic surfactants which promoted good wetting and suspension properties. However, detailed formulation analysis of the cleaning constituents is not available from the manufacturer and the subsequent influences of each component on cleaning cannot be easily investigated. A detailed investigation into the influence of a surfactant on cleaning the deposit is given in Section 5.13.

5.11.4 Effect of *Metaflux Stark* Cleaner temperature upon wheat starch deposit removal

The influence of the temperature of *Metaflux Stark* on the cleaning efficiency was investigated under its optimum concentration conditions isolated from the previous section. The experiments presented were performed at a cleaning concentration of 0.5 wt% *Metaflux Stark* at 40, 45, 50, 55, 60, 65 and 70°C, at a fluid velocity 0.33 m/s over a 25 minute cleaning duration (Figure 5.46).

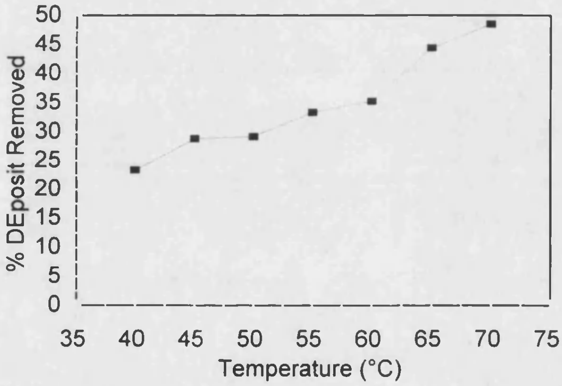


Figure 5.46: Temperature sweep for 0.5 wt% *Metaflux Stark* used for cleaning a 2 mm wheat starch deposit sample over a 25 minute duration at a velocity of 0.33 m/s.

5.11.4.1 *Discussion of results*

Figure 5.46 shows that deposit removal using *Metaflux Stark* cleaner was temperature dependant under the conditions investigated: As the temperature was increased the overall removal of deposit increased, although no clear cleaning temperature optimum is clear over the range studied.

It is apparent that *Metaflux Stark* performed better than its acid counterpart. This may be due to the increased wetting ability of the commercial cleaner.

5.12 THERMOPHILIC ENZYME AND DIASTASE

5.12.1 Effect of Diastase concentration upon wheat starch deposit removal

Experiments were performed at concentrations of 0.05, 0.1, 0.25, 0.5, 0.6, 1 wt% of the enzyme diastase. A temperature of 50°C and Reynolds number = 7380, (velocity = 0.33 m/s) were employed. Results are presented in Figure 5.47.

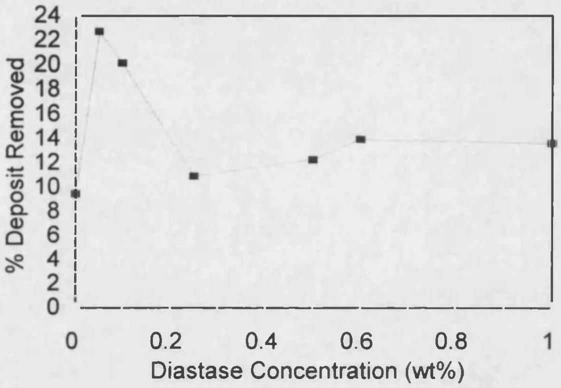


Figure 5.47: Overall diastase concentration sweep for the cleaning of a 2 mm wheat starch deposit over a 25 minute duration at 50°C, 0.33 m/s (Re = 7380), showing the existence of a concentration optimum at 0.05 wt% (pH = 6.1).

5.12.1.1 *Discussion of results*

An optimum diastase concentration was isolated for these experiments at 0.05 wt%, resulting in a deposit removal of 20% at 50°C and a flowrate of 4 l/min (velocity = 0.33 m/s) and buffered pH conditions (using sodium malate, pH = 6.9).

Cereal starches are more readily hydrolysed by α-amylase due to the lower content of crystalline structure and granule size (Ring *et al.* [1988]) and it is thought the enzyme initially hydrolyses amorphous regions of the starch granule (Franco *et al.* [1988]). Unlike α-amylase, β-amylase is an exo-acting enzyme which is able to hydrolyse α−1,4 linkages thereby liberating maltose. However, in both cases this degradation process is highly time dependant and this may explain the low cleaning efficiency observed for the 25 minute duration. It is likely that a much better cleaning efficiency would be achieved if a longer cleaning time had been allowed.

5.12.2 Effect of Diastase temperature upon wheat starch deposit removal

The influence of the temperature of diastase on the cleaning efficiency was investigated under the optimum concentration conditions isolated from the previous section. The experiments presented were performed at a cleaning concentration of 0.05 wt% diastase at 30, 40, 45, 50, 55, 60, 65, 70°C, at a fluid velocity 0.33 m/s over a 25 minute cleaning duration (Figure 5.48).

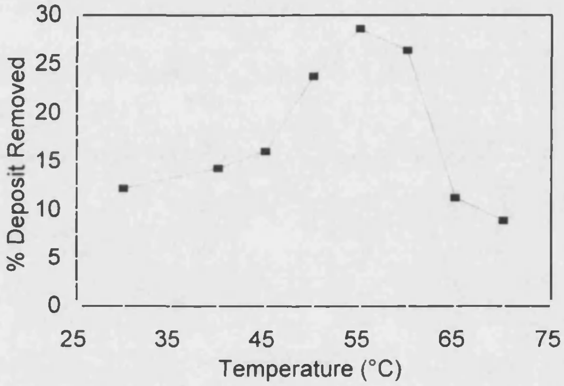


Figure 5.48: Temperature sweep for 0.05 wt% diastase used for cleaning 2 mm wheat starch deposit samples over a 25 minute duration at a velocity of 0.33 m/s (pH = 6.1).

5.12.2.1 *Discussion of results*

Figure 5.48 depicts the existence of an optimum temperature at 55°C under these flow conditions. An increase in temperature beyond this optimum yields a decrease in overall cleaning efficiency. This decrease may be attributed to the denaturation of the α- and β- amylases at the higher temperatures.

5.12.3 Effect of thermophilic α-amylase concentration upon wheat starch deposit removal

Experiments were performed at concentrations of 0.05, 0.1, 0.25, 0.5, 0.6, 1 wt% of the thermophilic α-amylase. A temperature of 60°C and Reynolds number = 8605, (velocity = 0.33 m/s) were employed. Results are presented in Figure 5.49.

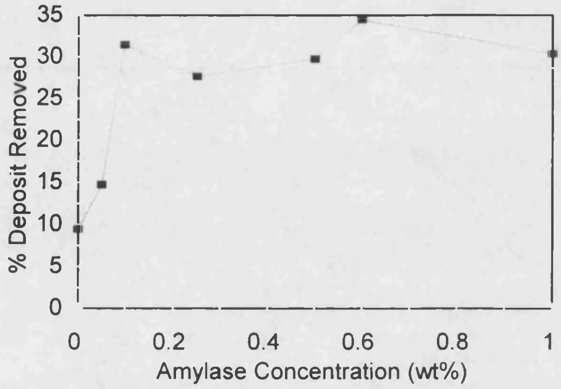


Figure 5.49: Overall thermophilic α-amylase (*Optiamyl*) concentration sweep for the cleaning of a 2 mm wheat starch deposit over a 25 minute duration at 60°C, 0.33 m/s (Re = 8605), pH = 7.0

5.12.3.1 *Discussion of results*

Although no distinct concentration optimum can be identified for the results obtained under these thermohydraulic conditions, it can be concluded that a minimum concentration of 0.1 wt% *Optiamyl* is required for effective deposit removal (~30% removal). Again, due to the tenacity of the deposit considered, greater cleaning efficiencies were not observed.

According to the suppliers, the optimum conditions for cleaning efficiency are influenced by the concentration of the substrate, the pH and the availability of calcium. A pH of 7 was maintained for the experiments performed but it is claimed that lower pH values allow a reduction in temperature and time required for cleaning. These factors were not investigated in detail.

An SEM study of the deposit after cleaning with *Optiamyl* is presented in Section 5.17.

5.12.4 Effect of thermophilic α-amylase temperature upon wheat starch deposit removal

The influence of the temperature of *Optiamyl* on the cleaning efficiency was investigated at a concentration of 0.1 wt%. The experiments presented were performed at temperatures of 50, 55, 60, 65, 70, 75, 80°C, at a fluid velocity 0.33 m/s over a 25 minute cleaning duration (Figure 5.50).

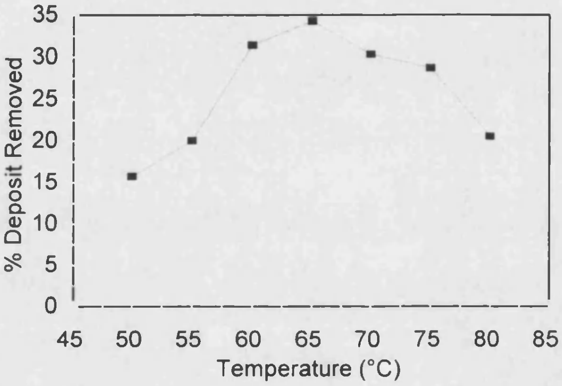


Figure 5.50: Temperature sweep for 0.1 wt% *Optiamyl* used for cleaning 2 mm wheat starch deposit samples over a 25 minute duration at a velocity of 0.33 m/s (pH = 7.0).

5.12.4.1 *Discussion of results*

An optimum temperature for removal is apparent from the results depicted in Figure 5.50 at 65°C under these flow conditions. Temperatures in excess of this lead to a significant decrease in overall cleaning efficiency due to the inactivation of the enzyme. The manufacturer claims that total inactivation of *Optiamyl* is achieved by increasing the temperature above 95°C for 10 to 25 minutes although this statement was not tested experimentally.

5.13 NON-IONIC SURFACTANT

5.13.1 Effect of $C_{9\text{-}11}E_6$ concentration and temperature upon wheat starch deposit removal

The solubility behaviour of the surfactant is anomalous in that as the temperature is increased a value is reached at which there is a sudden increase in solubility and the material becomes very highly soluble. This is referred to as the Kraft temperature and occurs at the temperature at which the solubility becomes equal to the cmc.

In the cleaning experiments performed, a two component system is formed between the surfactant and the water. As soon as the micelles are formed, the solubility becomes very high. In dilute solutions the micelles are randomly distributed throughout the solution phase. As the concentration is increased, however, changes occur in the system and organised systems are frequently found. These are described by Tadros [1983] as:

1. the hexagonal phase (middle) - composed of cylindrical units, hexagonally close-packed,
2. the viscous-isotropic phase - composed of spherical units in a body-centred cubic arrangement,
3. the lamellar phase (neat) - composed of sheets of molecules in a bimolecular packing with the head-group exposed to the water layers in between them.

The concentration and temperature domains over which these phases are formed, the so-called lyotropic mesomorphic phases vary for different surfactants. On heating aqueous solutions of nonionic surfactants they separate into two liquid phases, one rich in water and the other rich in surfactant. This is noticeable in practice by the fact that at a certain temperature the solution suddenly goes cloudy; referred to as the cloud point. It is usually determined just above the cmc.

The monomer structure of the nonionic surfactant defines its properties as a function of temperature; it exhibits reverse solubility with increasing temperature (Espig [1997]). In addition, the applied concentration will also affect the packing and shape of the micelles formed. For these reasons, the effects of temperature and concentration have been studied in conjunction for this particular cleaner.

The effect of $C_{9-11}E_6$ concentration with temperature has been studied in detail at a flowrate of 4 l/min, 0.33 m/s; representing fully developed turbulent flow. Analysis has been performed at temperatures between 20 - 80°C, over concentrations of 0 (water), 0.5, 1, 1.5, 2, 2.5, 3.5, 4, 5, 6, 8, 10 and 15 wt%. The initial results are presented as overall concentration and temperature sweeps at fixed thermohydraulic operating conditions over a 25 minute cleaning duration for 2 mm depth wheat starch deposit samples. Subsequent results are presented in a kinetic removal format in order of increasing concentration and the results are discussed.

The cloud point temperature for the $C_{9-11}E_6$ is 57°C and the critical micelle concentration is between 0.018-0.015 v/v% at 30 to 80°C respectively. The average value results for the cleaning effect of various concentrations of $C_{9-11}E_6$ at a temperature of 70°C over a 25 minute cleaning duration are presented in Figure 5.51.

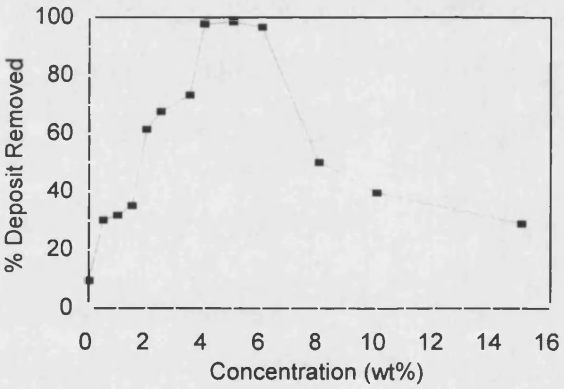


Figure 5.51: Overall $C_{9-11}E_6$ concentration sweep for the cleaning of a 2 mm wheat starch deposit over a 25 minute duration at 70°C, 0.33 m/s (Re = 9875)

5.13.1.1 *Discussion of overall concentration sweep at 70°C*

The shape of the graph in Figure 5.51 implies the existence of an optimum concentration for removal at 4 wt% under these thermohydraulic conditions. The influence of temperature and concentrations will be studied in greater detail as a function of time (i.e. kinetically), at a fixed flowrate to obtain a clearer picture of the dominating influencing factors on removal under each of the conditions studied in the following sections.

5.13.1.2 *Discussion of kinetic removal effects at a $C_{9-11}E_6$ concentration of 0.5 wt%*

Figure 5.52 displays the change in the removal kinetics with increasing $C_{9-11}E_6$ temperature. At 20°C the chemical contribution to removal is more significant to removal than the thermal effect. However, operating at a higher temperature of 60°C has a similar removal curve but has shifted the significance to a thermal rather than a chemical effect.

Intermediate temperatures (35 and 50°C), below the cloud point temperature of 57°C, are noted to have similar cleaning efficiencies over the time span considered (~15% removal), but of a significantly lower order than 20 and 60°C respectively.

It is observed that a significant proportion of the deposit remains intact on the stainless steel test-plate even after a 25 minute cleaning period. This illustrates the tenacious nature of the soil-substrate bonds.

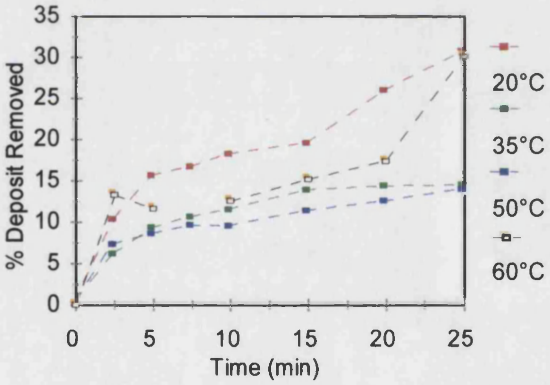


Figure 5.52: The temperature effect on 0.5 wt% $C_{9-11}E_6$ for cleaning a 2 mm wheat starch deposit at 4 l/min, 0.33 m/s.

5.13.1.3 *Discussion of kinetic removal effects at a $C_{9-11}E_6$ concentration of 1.5 wt%*

Figure 5.53 displays the change in the removal kinetics with increasing $C_{9-11}E_6$ temperature at a concentration of 1.5 wt%. The removal curves at each temperature appear to resemble a sigmoidal pattern: the shape of this curve is a strong function of temperature. Large increases in the cleaning rate over certain time intervals on the graph may be attributed to removal occurring in aggregate pieces in the order of 2-3 mm in length. The visualisation experiments performed (Section 5.17) describe the cleaning process in greater detail and provide important clues to the mechanisms involved in the removal process.

At 20°C the chemical contribution to removal is similar to that for the thermal effect observed at 70°C. Temperatures of 20 and 40°C, which are below the cloud point temperature of 57°C are noted to have a better cleaning efficiency over the time considered. The solubility is better below the cloud point and therefore there is more surfactant available below 57°C to do the job. However, higher temperatures aid removal in the cleaning process.

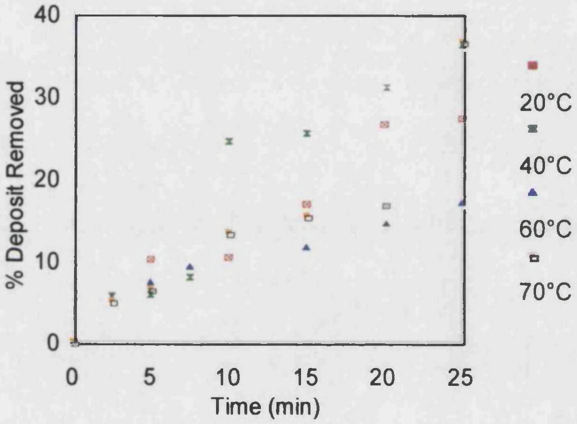


Figure 5.53: The temperature effect on 1.5 wt% $C_{9-11}E_6$ for cleaning a 2 mm wheat starch deposit at 4 l/min, 0.33 m/s.

5.13.1.4 *Discussion of kinetic removal effects at a $C_{9-11}E_6$ concentration of 4 wt%*

The effect of temperatures between 50-70°C were studied at a concentration of 4 wt% using a velocity of 0.33 m/s and the results are summarised in Figure 5.54.

The shapes of the removal curves are similar to those described in section 5.13.1.3 although the overall cleaning efficiency is greater at this concentration.

Initially, the cleaning rate is low for all temperatures for the first 10 minutes before rising to a maximum and then declining towards the end of the cleaning period. The induction period is likely to be caused by the time required for the surfactant to penetrate the deposit and result in any significant degree of cleaning to be observed. A cleaning temperature optimum exists above the cloud point under these conditions at 60°C, resulting in a 98% cleaning efficiency over the 25 minutes. It is noticeable that increasing the thermal effect further by 20°C to 80°C has little overall effect on the cleaning efficiency.

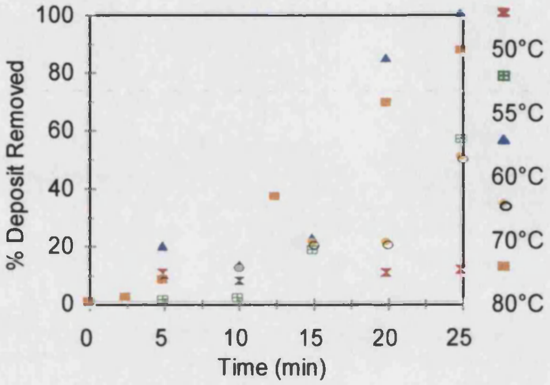


Figure 5.54: The temperature effect on 4 wt% $C_{9-11}E_6$ for cleaning a 2 mm wheat starch deposit at 4 l/min, 0.33 m/s.

5.13.1.5 *Discussion of temperature effects at a $C_{9-11}E_6$ concentration of 10 wt%*

The effect of temperatures between 40-80°C at a concentration of 10 wt% using a velocity of 0.33 m/s over a 25 minute cleaning duration were studied and the results are summarised in Figure 5.55. An optimum temperature for removal is apparent for these results below the cloud point at 50°C, under these flow conditions. Temperatures in excess of this lead to a significant decrease in overall cleaning efficiency; probably due to changes in the morphology of the deposit subjected to high temperature $C_{9-11}E_6$ cleaning solution. This will be investigated further in Section 5.17.

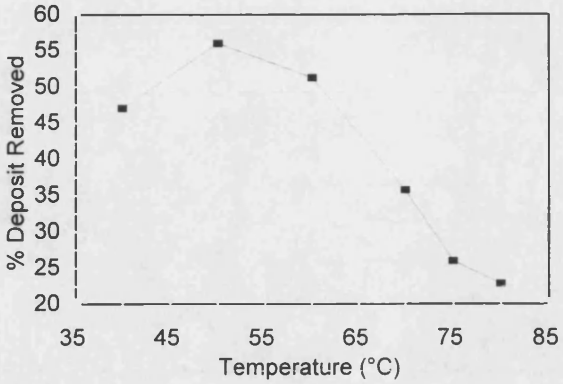


Figure 5.55: The temperature effect on 10 wt% $C_{9-11}E_6$ for cleaning a 2 mm wheat starch deposit at 4 l/min, 0.33 m/s after a 25 minute cleaning duration.

5.13.1.6 *Discussion of kinetic removal effects at a $C_{9-11}E_6$ concentration of 15 wt%*

The effect of temperatures between 50-80°C were studied at a concentration of 15 wt% using a velocity of 0.33 m/s and the results are summarised in Figure 5.56.

The shapes of the removal curves are similar to those described in section 5.13.1.4 although the overall cleaning efficiency is lower at this concentration.

Initially, the cleaning rate is low for all temperatures for approximately 10 minutes before rising to a maximum and then declining towards the end of the cleaning period. A cleaning temperature optimum exists under these conditions at 50°C, resulting in a 95% cleaning efficiency over the 25 minutes. It is noticeable that increasing the thermal effect further by 10°C to 60°C (above the cloud point) causes a significant decline in the overall cleaning efficiency effect.

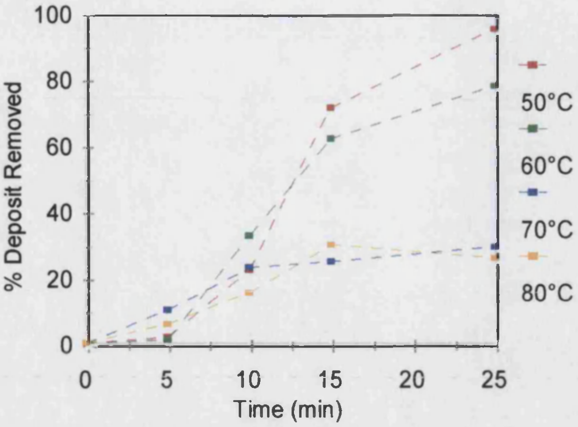


Figure 5.56: The temperature effect on 15 wt% $C_{9\text{-}11}E_6$ for cleaning a 2 mm wheat starch deposit at 4 l/min, 0.33 m/s.

5.13.1.7 *Summary of concentration and temperature effects of $C_{9\text{-}11}E_6$*

The phase behaviour of the nonionic surfactants is very sensitive to temperature changes and on heating the $C_{9\text{-}11}E_6$ separates into two isotropic solutions. Simply from the head-group area-to-alkyl chain volume ratio (approximately 0.6), one expects the micellar growth to be easy (Espig [1997]). Furthermore, a micellar growth shape change sphere-rod-lamellae should be facilitated by a temperature increase. The cloud point seems generally to lie just above the upper stability limit of the hexagonal phase, which would point to a rod-lamellar transition in this range (Kling and Lange [1960]).

When a nonionic is mixed into water the hydroxy groups of the surfactant hydrate to form a voluminous sheath around the polar heads. The size of this sheath and tenacity with which this water is held determines at which interface the surfactant will concentrate and the strength of the interfacial film thus formed. Heating causes the dehydration of these polar groups and reduces the surfactant's solubility. The temperature at which this dehydration becomes visible in the form of solution turbidity (caused by surfactant molecules aggregating into larger micelles) is its "cloud point" (Vincent [1985]).

A nonionic surfactant is most effective when used up to about 10°C below and 20°C above its cloud point under its conditions of use. In this temperature range its interfacial concentration is maximised and polar groups are still sufficiently hydrated to form viscous interface-modifying film structured by lateral hydrogen bonding via intermediate water molecules.

Efficient wetting is obtained when the gas-liquid and solid-liquid interfacial tensions are minimised. The wetting efficiency can be quantified by contact angle determination. The surfactant is most efficiently wetted when the nonionic is barely soluble (i.e. on or above the cloud point) under the conditions of use.

5.13.2 Increasing the velocity

The influence of surfactant velocity upon removal has been investigated. A wide range of velocities have been studied (0.082 to 0.49 m/s) at 50°C and 4 wt% $C_{9-11}E_6$. Flowrates of 1, 2, 4, 5 and 6 l/min with Reynolds numbers of 1845, 3689, 7378, 9228 and 11067 respectively are presented in Figure 5.57.

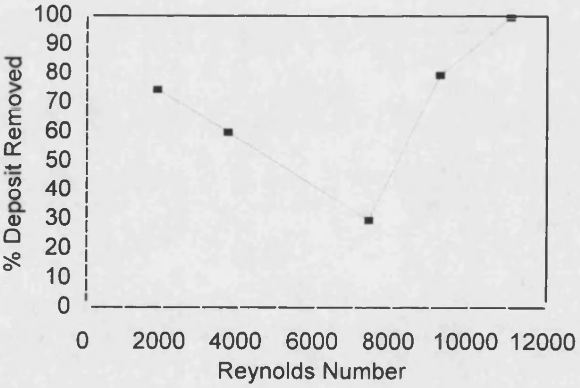


Figure 5.57: The velocity effect on 4 wt% $C_{9-11}E_6$ for cleaning a 2 mm wheat starch deposit at 50°C for 25 minutes.

5.13.2.1 *Discussion of removal effects due to velocity at a 4 wt% concentration of $C_{9-11}E_6$*

It is apparent from the results obtained that removal is a strong function of cleaning velocity for the thermo-hydraulic conditions studied over the 25 minute cleaning duration. It is also interesting to note that laminar flow conditions (Re<2000), are as effective for deposit removal as fully developed turbulent flow (Re~9000). Further increases in flow-rate and hence Reynolds number, resulted in an increase in overall deposit removal due to the greater influence of shear stress effects. An explanation for these trends are explained in mechanistic terms using the observations from the visualisation experiments in Section 5.17.

Figures 5.58 and 5.59 depict the kinetic cleaning curves obtained using a 4 wt% concentration of $C_{9-11}E_6$ at Reynolds numbers of 3689 and 11067. It is noted that significantly different cleaning curves are observed depending on the cleaning velocity applied. The shear forces are clearly more significant on the deposit when applying a surfactant solution as opposed to pure water. The cleaning kinetics observed are discussed further in Chapter 6 in the analysis of a cleaning model.

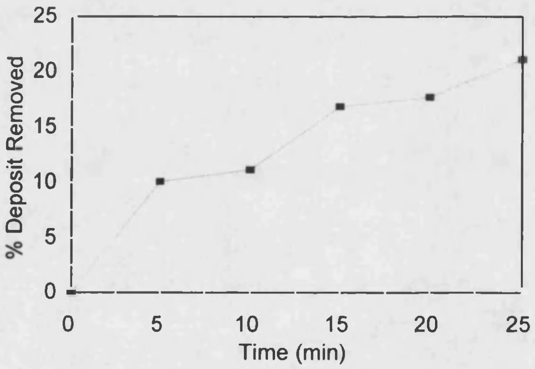


Figure 5.58: The velocity effect on 4 wt% $C_{9-11}E_6$ for cleaning a 2 mm wheat starch deposit at 2 l/min, 0.16 m/s, 50°C (Re = 3689).

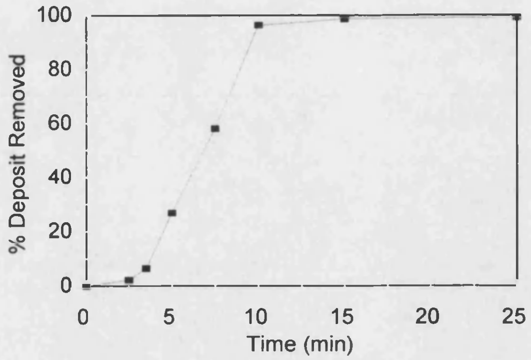


Figure 5.59: The velocity effect on 4 wt% $C_{9\text{-}11}E_6$ for cleaning a 2 mm wheat starch deposit at 6 l/min, 0.49 m/s, 50°C (Re = 12900).

5.14 VARIATION IN DEPOSIT THICKNESS

The depth of a deposit is an important parameter in the cleaning process (Section 1.5). The effect of increasing the wheat starch deposit thickness to 3 mm upon removal has been determined at 70°C, 4 l/min for concentration sweeps of sodium hydroxide, nitric acid and the $C_{9\text{-}11}E_6$ for a 25 minute cleaning duration. Results have been presented for the standard surface coverage of 1635 g/m^2 for a thickness of 3 mm in Figures 5.60-5.62.

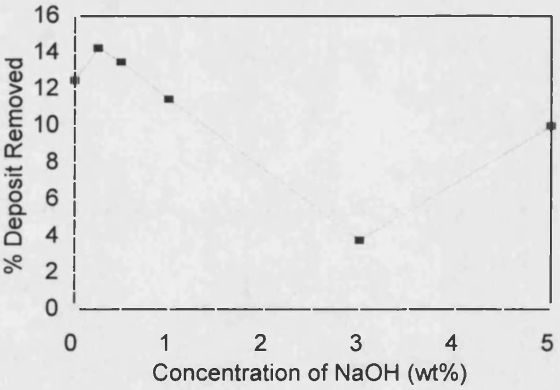


Figure 5.60: Concentration sweep using sodium hydroxide and its cleaning effect on a 3 mm wheat starch deposit over a 25 minute duration.

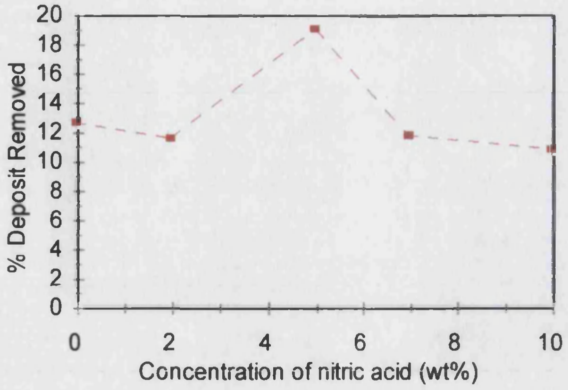


Figure 5.61: Concentration sweep using nitric acid and its cleaning effect on a 3 mm wheat starch deposit over a 25 minute duration.

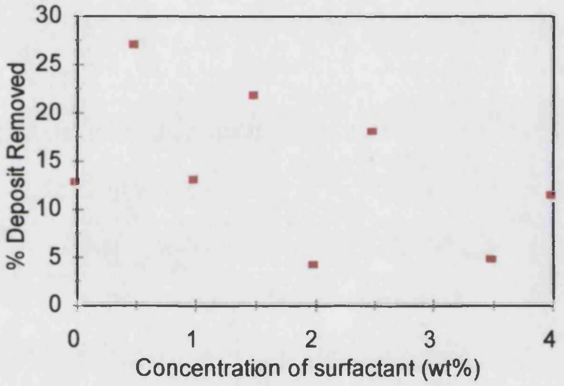


Figure 5.62: Concentration sweep using $C_{9\text{-}11}E_6$ and its cleaning effect on a 3 mm wheat starch deposit over a 25 minute duration.

5.14.1 Discussion of results

Increasing the surface coverage of wheat starch deposit from 1501 to 1635 g/m^2 has a significant effect on the overall cleaning efficiency of the cleaners studied under these thermohydraulic conditions. It is noted that cleaning efficiency decreases significantly: confirming the fact that the soil-soil bonds are very strong and a dependency on deposit thickness on overall efficiency exists. It is likely from these results that the cleaning process is diffusion related and a detailed investigation of the mechanisms involved is discussed in Chapter 6.

Concentration optima coincide for the caustic and nitric cleaners to the corresponding values determined for a 2 mm wheat starch deposit (0.5 wt% and 5 wt% respectively). However, no clear concentration optimum is apparent for $C_{9-11}E_6$ under these conditions suggesting a complex mechanism is involved (Chapter 6).

5.15 AGEING DEPOSIT

Cleaning recommendations always emphasise that surfaces should be cleaned as soon as possible. Smith [1969] pointed out that unheated sugar and fruit soils can be easily cleaned, provided they have not been allowed to dry. The ageing effect of oil-containing soils in the cleaning of textile fibres is well known (Untermohlen & Walace [1974], Durham [1961]). Bourne & Jennings [1961][1963], showed that tristearin, deposited on stainless steel, exists in two chemically identical forms that are removed at different rates, and that the ageing effect involves transition of the fast-removal soil species to the slowly removed form. Similar observations have been reported regarding milk soils (Burton [1964]).

An SEM study of the ageing effect of the baked wheat starch deposit was performed. The results are depicted in Figures 5.63(a)-(c).

At low magnification it is apparent that the deposit surface has a number of cracks and crevices up to 1 μm wide. (Figure 5.63(a)). Closer examination of the surface topology depicts an undulating dune-like deposit structure with a degree of starch granule damage present (Figure 5.63(b) and (c)). In addition the platelet structure of the deposit is intertwined with smaller matrix components (Figure 5.63(c)).

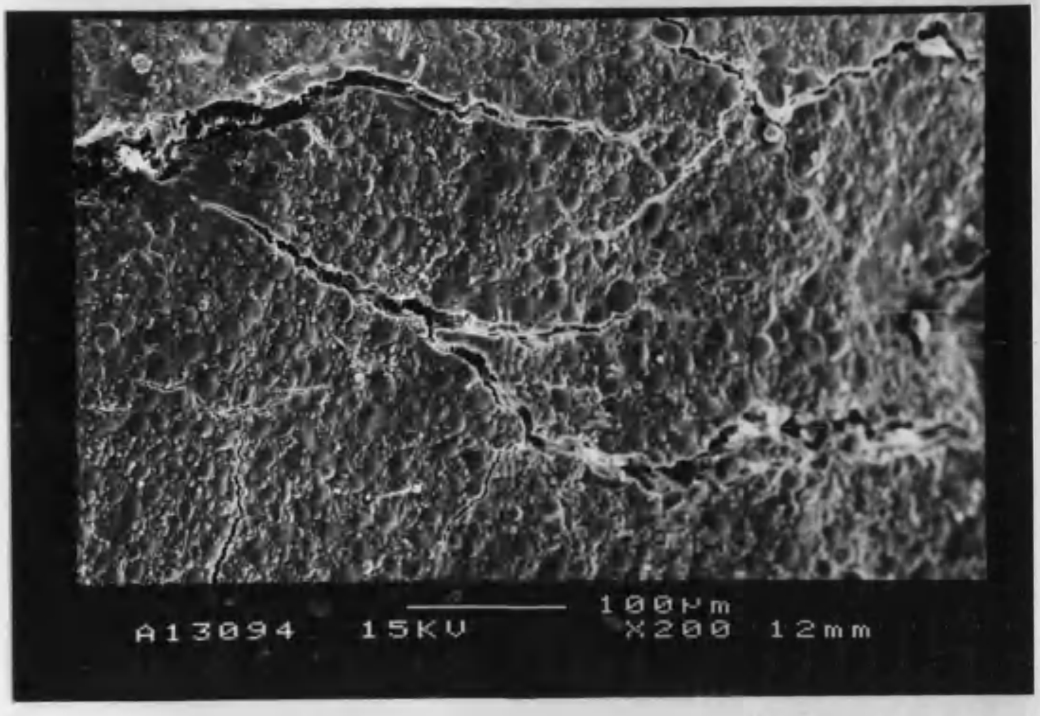


Figure 5.63(a): SEM micrograph of aged wheat starch deposit (magnification x200)

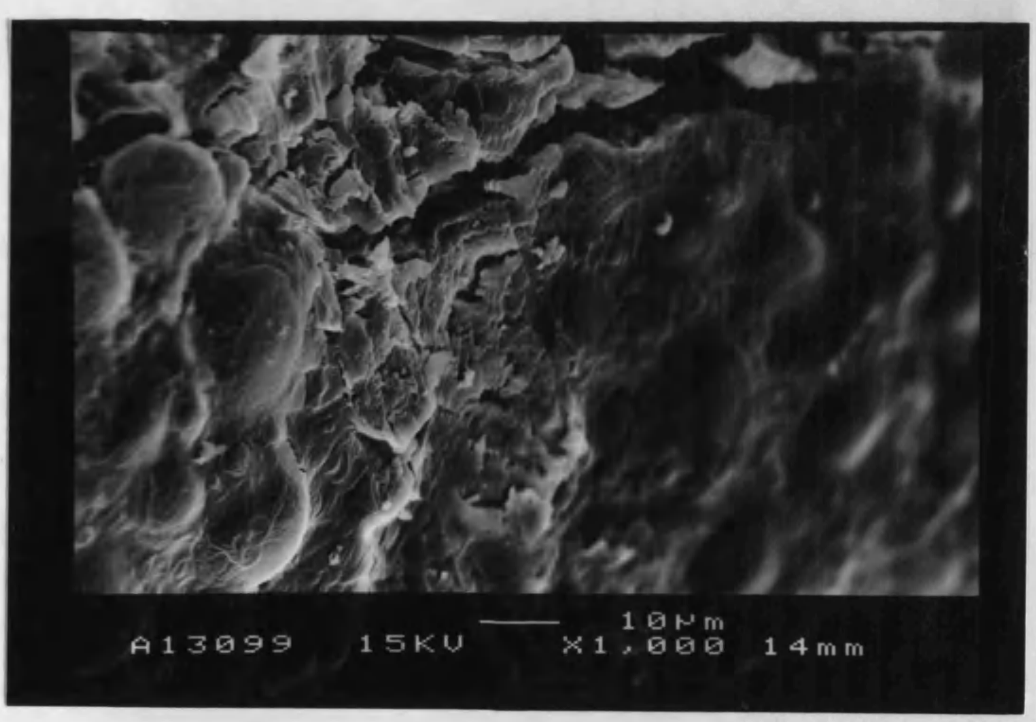


Figure 5.63(b): SEM micrograph of aged wheat starch deposit (magnification x1000)

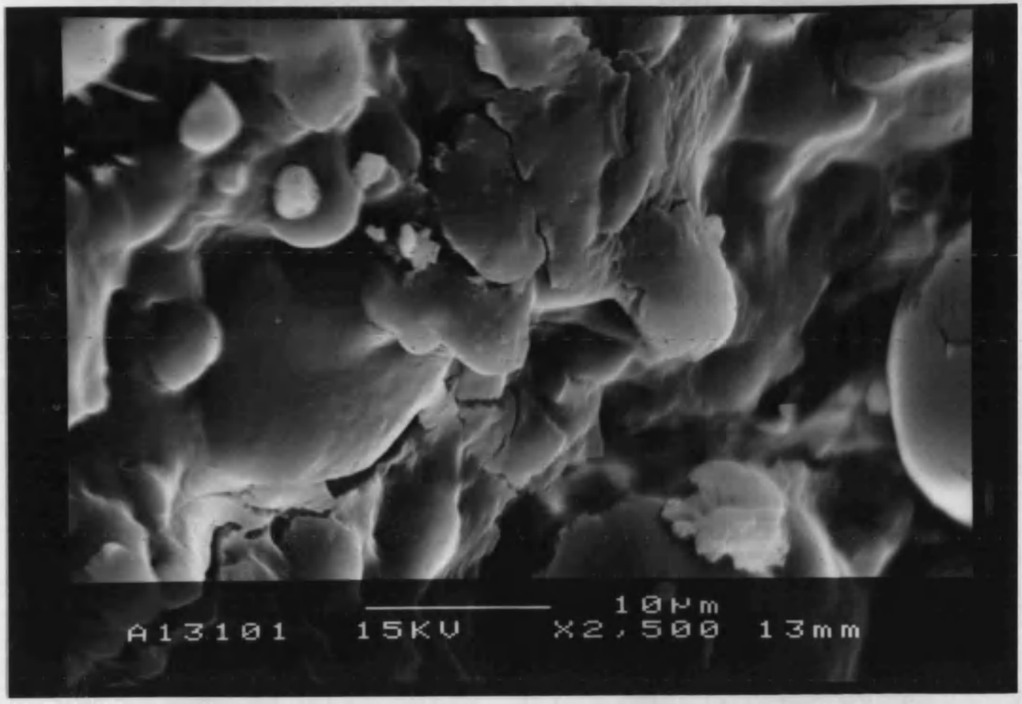


Figure 5.63(c): SEM micrograph of aged wheat starch deposit (magnification x2500)

5.16 SUMMARY

- Increasing rinse water temperature has minimal effect on cleaning, regardless of water hardness.
- Increasing Reynolds numbers for rinsing is directly proportional to the cleaning efficiency observed.
- An optimum concentration and temperature optimum of 0.5 wt% and 50°C were isolated for sodium hydroxide under fully developed turbulent flow conditions (velocity =0.33 m/s). Increasing the cleaning velocity had a significance on the overall cleaning efficiency observed.
- Addition of 2 g/l of EDTA to 0.5 wt% sodium hydroxide at 50°C, had minimal effect on the overall cleaning efficiency.
- Addition of *Synperonic LF/CS 1000* to 0.5 wt% NaOH solution resulted in an overall improvement in cleaning efficiency and an optimum concentration was isolated at 0.01 wt%.

- An optimum nitric acid concentration was isolated at 5wt% for a cleaning velocity of 0.33 m/s, although no temperature optimum was determined. In addition, an increase in the fluid velocity caused a subsequent increase in the cleaning efficiency.
- An optimum detergent concentration for the *Micro-90* exists at 5 wt% and although no cleaning temperature optimum was clear, it is apparent that the cleaning efficiency is temperature dependent variable.
- An optimum detergent concentration for the acidic Metaflux Stark cleaner was observed at 0.5 wt% and a strong temperature dependency trend was discovered.
- An optimum concentration of 0.05 wt% diastase and a temperature of 55°C was isolated for a cleaning velocity of 0.33 m/s.
- An optimum concentration of 0.1 wt% *Optiamyl* and a temperature of 65°C was isolated for a cleaning velocity of 0.33 m/s.
- A strong dependency of concentration, temperature and cleaning velocity parameters exist for the use of the nonionic surfactant $C_{9\text{-}11}E_6$.
- Cleaning efficiency decreases significantly with increasing depth of wheat starch deposit.
- Deposit morphology changes dramatically with time.

5.17 QUALITATIVE EVALUATION OF CLEANING

To supplement the results obtained from the quantitative data, and obtain further information regarding the mechanisms involved in the cleaning process a series of qualitative experiments were performed. Observations included:

I. Scanning Electron Microscopy (SEM), to show how the deposit structure changed on contact with the cleaning chemicals.

II. Cleaning process visualisation using advanced video photography to determine any change in deposit structure with cleaning time.

5.17.1 SEM Study

Scanning electron microscopy was employed to study the effect of various cleaning agents on the deposit structure. The samples were prepared using the techniques described in section 4.6.3. The sample specimens were viewed using a JSM-T330 and JSM-6310 Scanning Electron Microscope in the Electron Optics Centre, University of Bath.

In order to ensure that the effects viewed were genuine and not merely artefacts of the sample preparation technique they were prepared using a cryogenic treatment. The main objective of this study was to witness the chemical cleaning effect upon the deposit morphology and not examine the temperature or flow effects. For this reason, the samples were immersed in beakers of cleaning solution at specified concentrations and temperatures for a contact time of 25 minutes. Samples were then rinsed with reverse osmosis (RO) water, before undergoing the necessary treatment process for SEM analysis.

5.17.1.1 *0.5 wt% sodium hydroxide at 50°C*

SEM studies were carried out on a deposit contacted with 0.5 wt% NaOH at 50°C for 25 minutes. These conditions represented the optimum conditions observed for cleaning under flow conditions (Section 5.9).

Figures 5.64(a) depicts the structure has changed dramatically on contact with the sodium hydroxide: a cellular honeycomb structure in which a thin matrix of binding material surrounds large holes c.a. 1-3 μm across (Figure 5.64(b)).

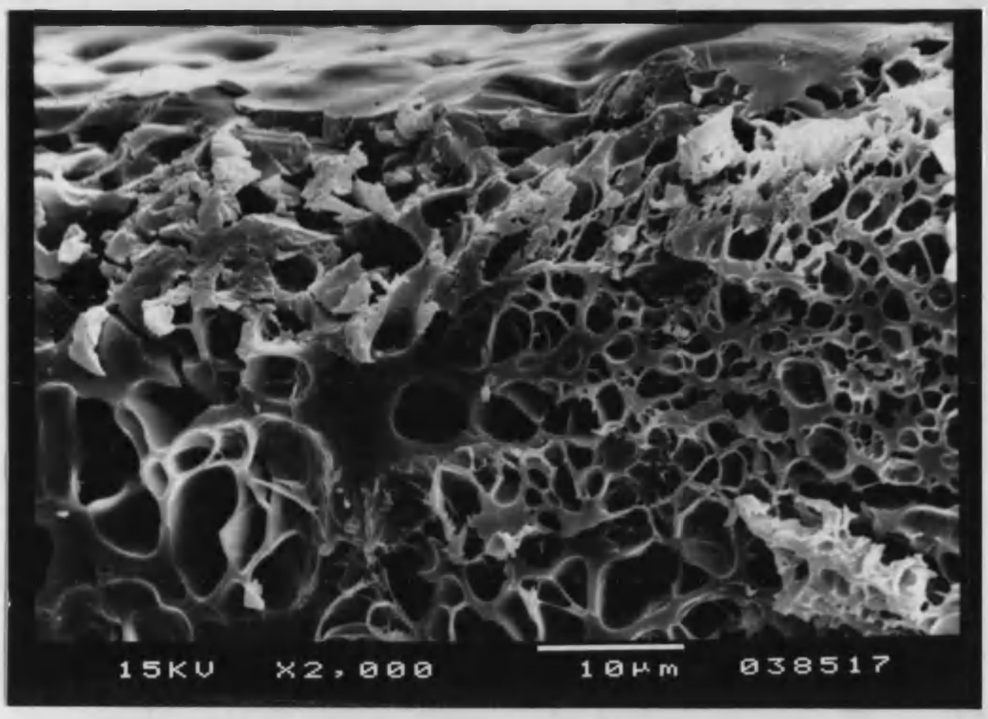


Figure 5.64(a): SEM micrograph of wheat starch deposit contacted with 0.5 wt% sodium hydroxide at 50°C for 25 minutes (magnification x2000)

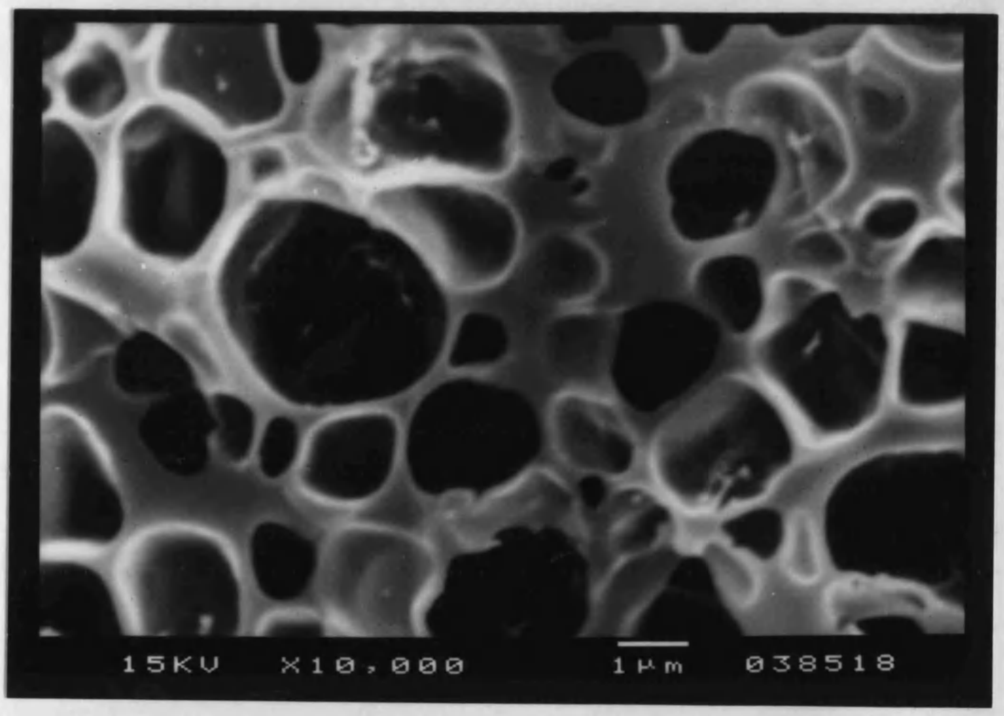


Figure 5.64(b): SEM micrograph of wheat starch deposit contacted with 0.5 wt% sodium hydroxide at 50°C for 25 minutes (magnification x10000)

5.17.1.2 *5 wt% nitric acid at 70°C*

SEM studies were carried out on a deposit contacted with 5 wt% nitric acid at 70°C for 25 minutes. These conditions represented the optimum conditions observed for cleaning under flow conditions (Section 5.10).

Figures 5.65(a) depicts the surface structure resembles that obtained in the previous section using sodium hydroxide. Although the majority of the starch granules are damaged they remain resistant to the nitric acid hydrolysis treatment under these conditions (Figure 5.65(b)). This explains the low removal rate obtained over this time-span. In addition the structure is bound together by a gluten matrix of a similar honeycomb network observed in the previous section (Figure 5.65(c)).

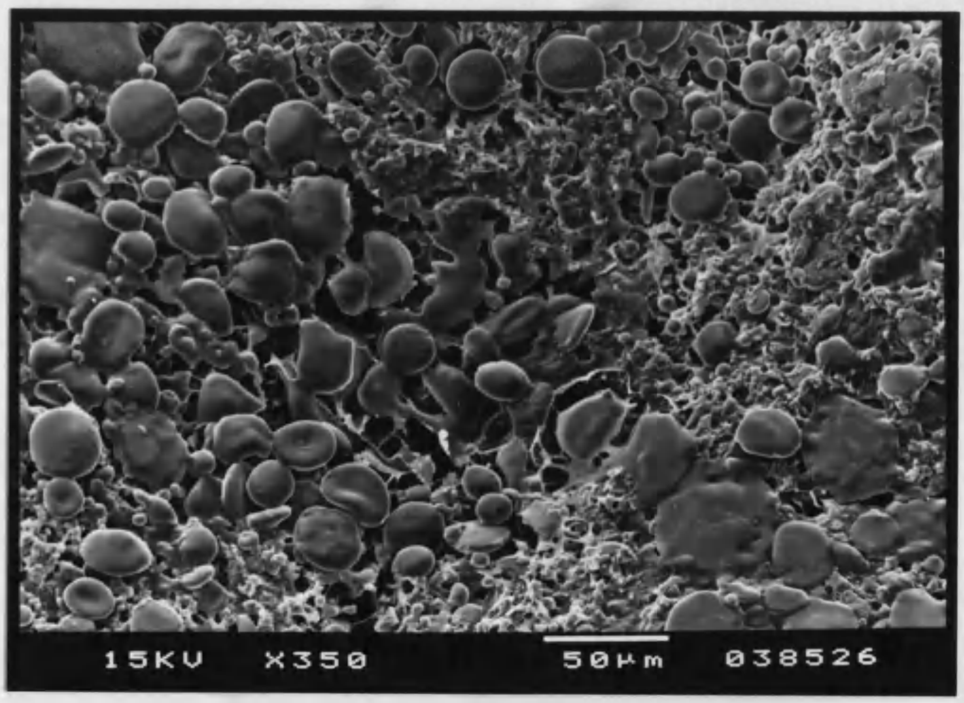


Figure 5.65(a): SEM micrograph of wheat starch deposit contacted with 0.5 wt% nitric acid at 70°C for 25 minutes (magnification x350)

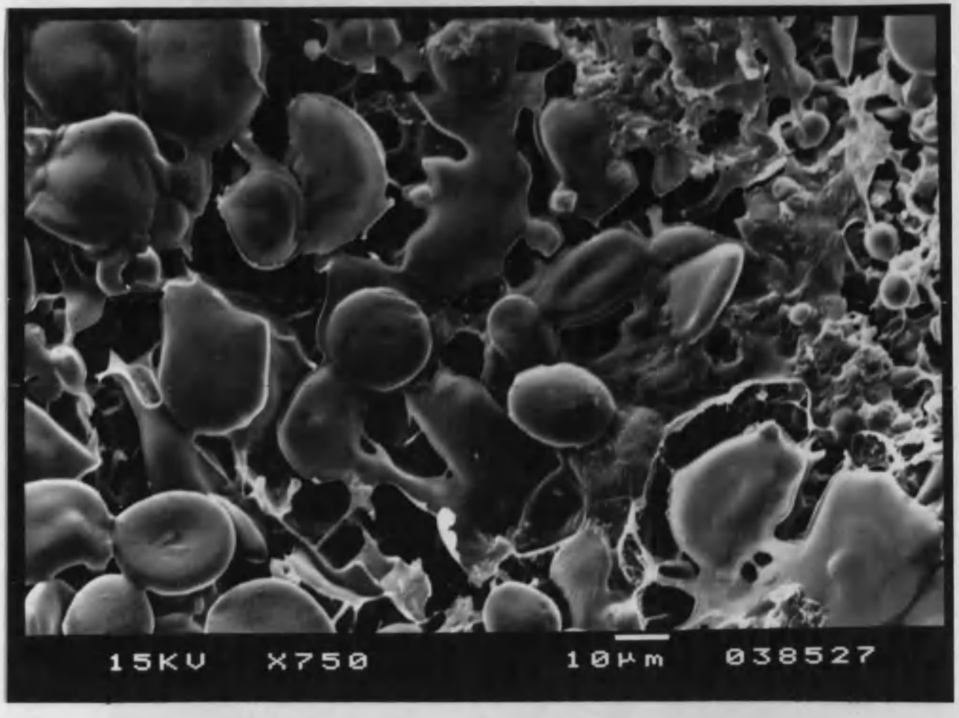


Figure 5.65(b): SEM micrograph of wheat starch deposit contacted with 0.5 wt% nitric acid at 70°C for 25 minutes (magnification x750)

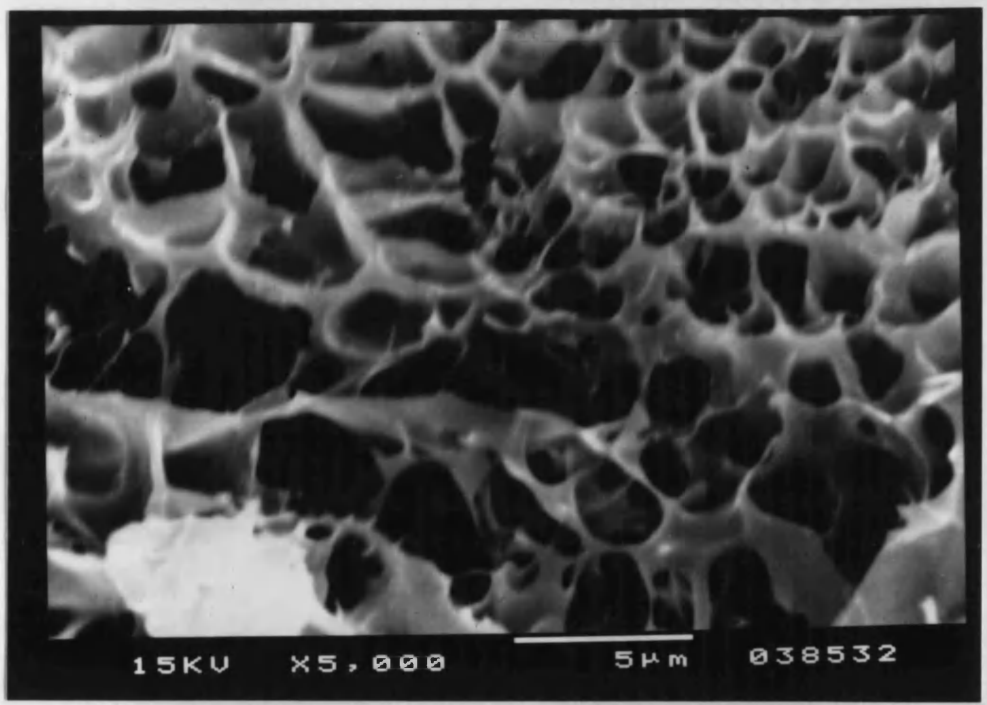


Figure 5.65(c): SEM micrograph of wheat starch deposit contacted with 0.5 wt% nitric acid at 70°C for 25 minutes (magnification x5000)

5.17.1.3 *0.1 wt% thermophilic α–amylase (*Optiamyl*) at 65°C (pH = 7)*

SEM studies were carried out on a deposit contacted with 0.1 wt% thermophilic α–amylase (*Optiamyl*) at 65°C (pH = 7) for 25 minutes. These conditions represented the optimum conditions observed for cleaning under flow conditions (Section 5.12).

During α-amylolysis, the hard (most crystalline) parts of the starch granules are less digested than the soft parts. The susceptibility of starch granules can be classified by the intensity and manner by which the granules are eroded and corroded (Gallant *et al.* [1992]). Most of the starch granules are first hydrolysed superficially as shown in Figure 5.66(a). In wheat starch granules there have specific susceptible zones which become pitted due to endocorrosion. The pits become enlarged and canals of endocorrosion sink into the granule. Then, numerous canals are randomly formed around the granules (Figure 5.66(b)).

Under SEM at high magnification and using better conditions for image resolution, the starch granules treated by this enzymic process appear to be composed of small, more or less spherical blocklets coming together tangentially. In the hard parts of the shells, blocklets may be up to 100 nm in diameter, whereas they are only 25 nm in the soft parts. This explains the particular resistance of these starch granules to hydrolysis.

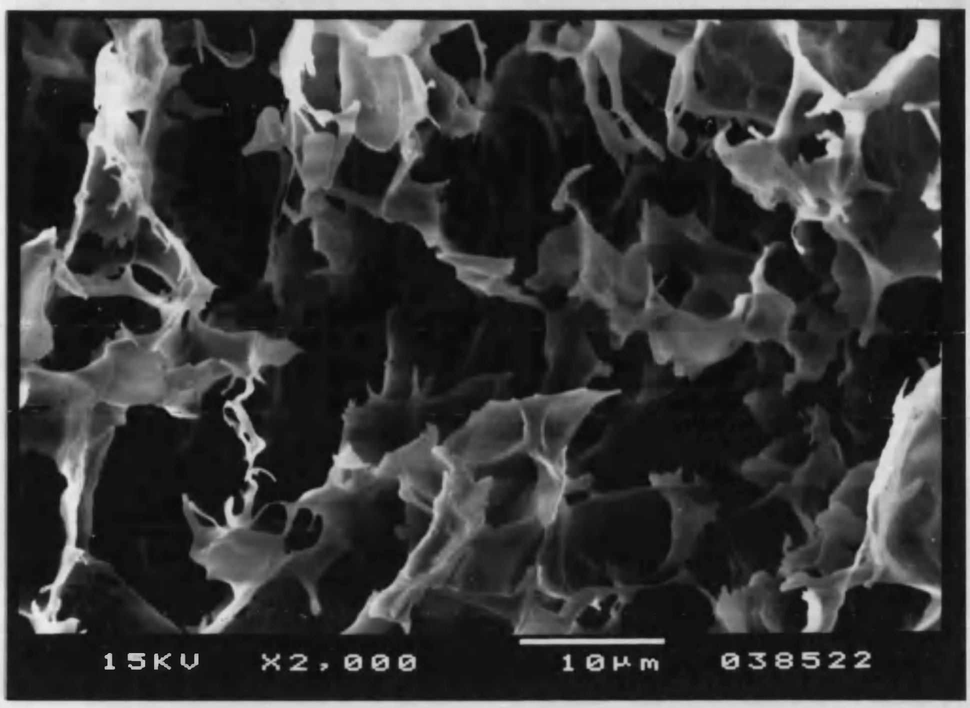


Figure 5.66(a): SEM micrograph of wheat starch deposit contacted with 0.1 wt% thermophilic α–amylase (*Optiamyl*) at 65°C (pH = 7) for 25 minutes (magnification x2000)

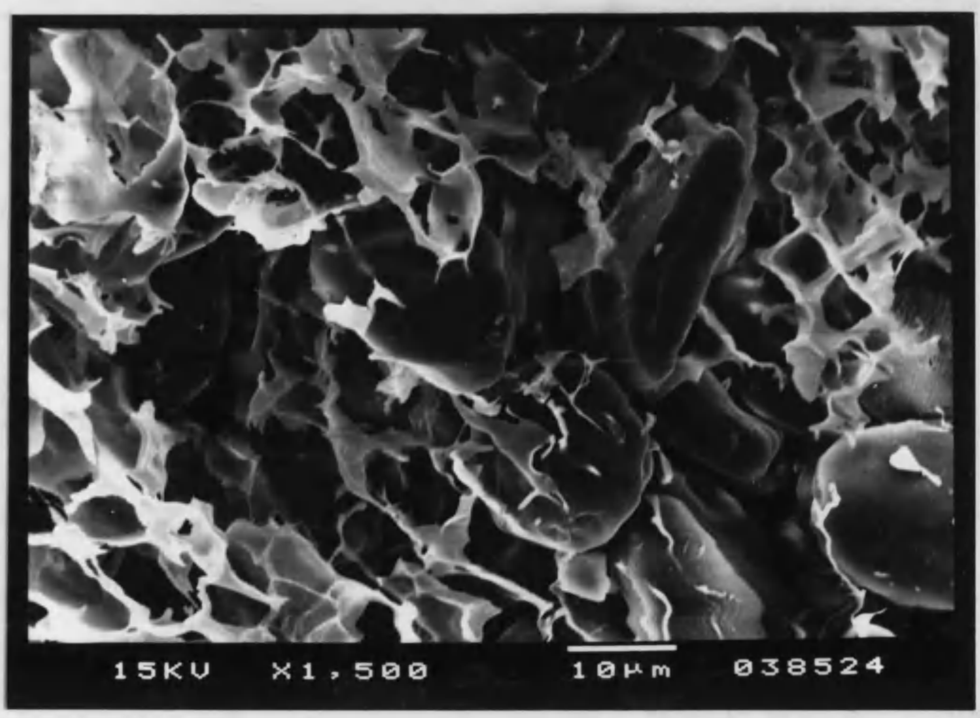


Figure 5.66(b): SEM micrograph of wheat starch deposit contacted with 0.1 wt% thermophilic α–amylase (*Optiamyl*) at 65°C (pH = 7) for 25 minutes (magnification x1500)

5.17.1.4 *4 wt% $C_{9-11}E_6$ concentration at 60°C*

SEM studies were carried out on a deposit contacted with 4 wt% $C_{9-11}E_6$ at 60°C for 25 minutes. These conditions represented the optimum conditions observed for cleaning under flow conditions (Section 5.13).

Figure 5.67(a) depicts the porous surface structure observed using SEM techniques at a magnification of 1000. It is noticeable that a significant number of apertures exist (~1-5 μm diameter) in the topographic surface structure (Figure 5.67(b)). This provides an explanation for the swelling phenomena observed during the cleaning process and the penetrating/ wetting power of the surfactant under these conditions.

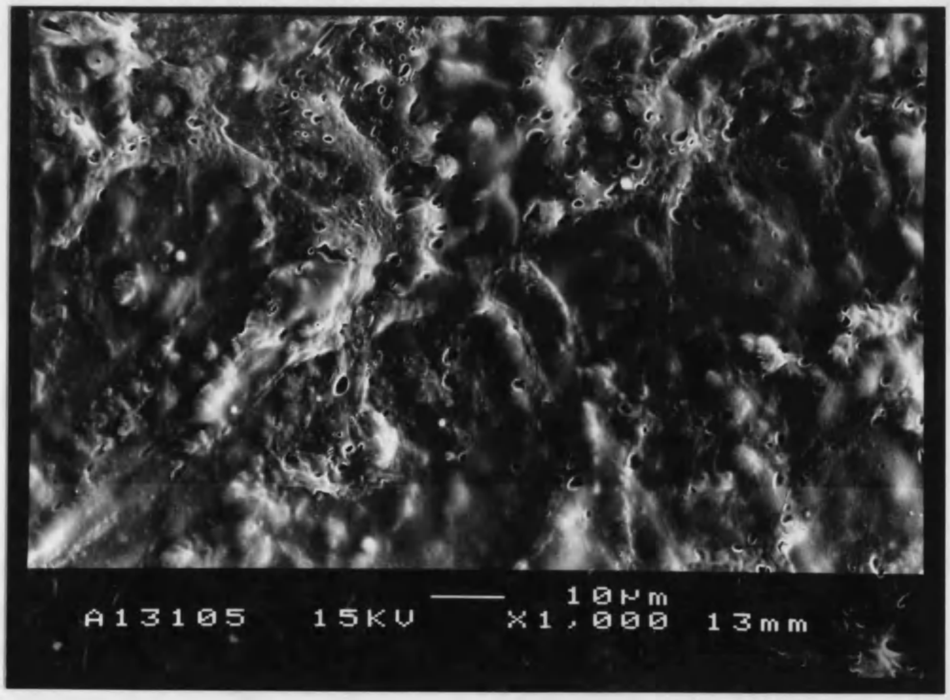


Figure 5.67(a): SEM micrograph of wheat starch deposit contacted with 4wt% $C_{9-11}E_6$ at 60°C for 25 minutes (magnification x1000).

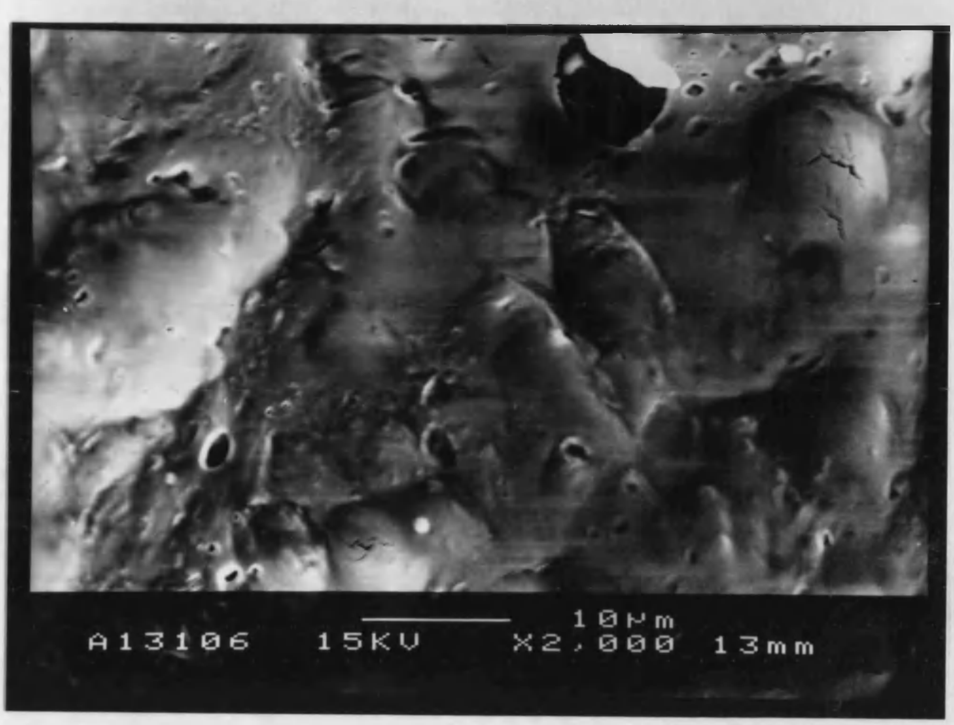


Figure 5.67(b): SEM micrograph of wheat starch deposit contacted with 4 wt% $C_{9-11}E_6$ at 60°C for 25 minutes (magnification x2000).

5.17.2 Process Visualisation

There has been little work published on the direct visualisation of sequence of events involved in the cleaning process for starch deposits. The experimental apparatus developed in this protocol allows the use of advanced video photography techniques to be applied without optical distortion by the use of a rectangular cross-sectioned glass cell (Section 4.5.3.2).

Fouled test-plates with a surface coverage of 1500 g/m^2 were positioned in the glass cell and the cleaning observed over a wide range of conditions.

5.17.2.1 *RO water at 50°C*

Figure 5.68(a)-(c) depict the effect of RO water on the wheat starch deposit. The water is applied at 50°C and 4 l/min.

It is clear from these photographs that no visible degree of removal is observed over the time span considered.

The starch deposit although of a uniform central profile has an uneven edge structure (Figure 5.68(a)). These regions remain intact during the rinsing process and although a degree of deposit swelling is apparent they represent a very tenacious soil-substrate bond.

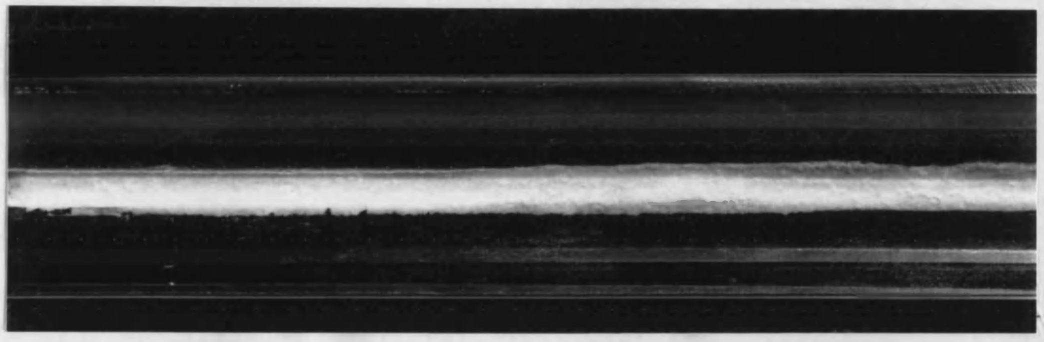


Figure 5.68(a): Photograph of wheat starch deposit contacted with RO water at 50°C and 4 l/min for 5 minutes.

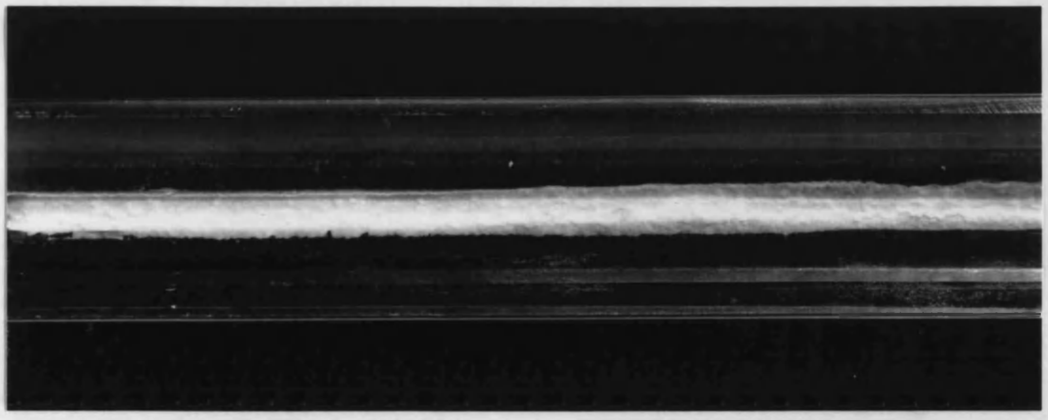


Figure 5.68(b): Photograph of wheat starch deposit contacted with RO water at 50°C and 4 l/min for 10 minutes.

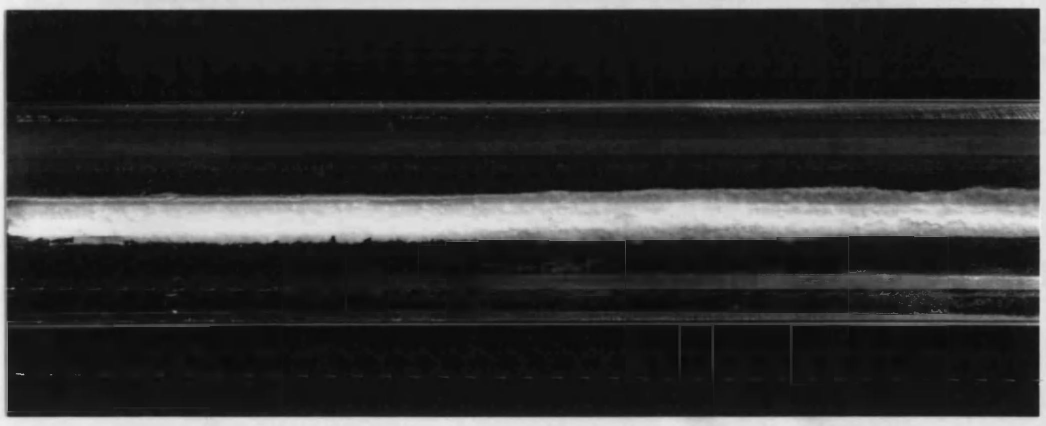


Figure 5.68(c): Photograph of wheat starch deposit contacted with RO water at 50°C and 4 l/min for 25 minutes

5.17.2.2 0.5 wt% *sodium hydroxide + 0.01 wt% Synperonic at 50°C*

The addition of 0.01 wt% *Synperonic LF/CS 1000* to 0.5 wt% NaOH solution was investigated at 50°C and a flow-rate of 4 l/min over a 50 minute duration (Figures 5.69(a)-(i)).

The direction of flow is from left to right. As the cleaning progresses it is clear that the removal is non-uniform: initially the deposit swells (swelling ratio of 2:1) indicating a reduction in the strength of the soil-soil bonds (Figure 5.69(b)), before removal occurs in aggregate lift-off from the channel.

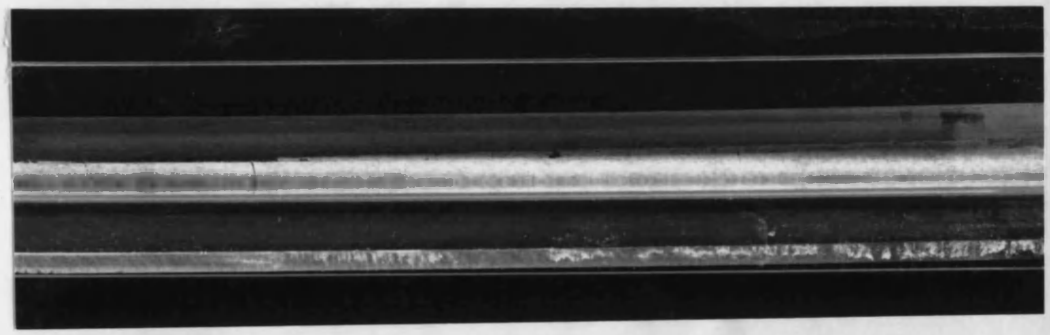


Figure 5.69(a): Photograph of wheat starch deposit contacted with 0.01 wt% *Synperonic LF/CS 1000* + 0.5 wt% NaOH at 50°C and 4 l/min for 1 minute.

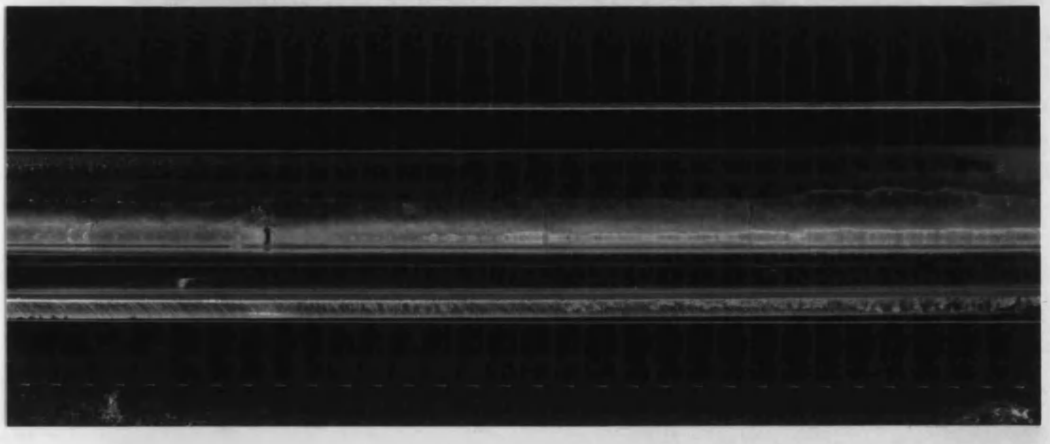


Figure 5.69(b): Photograph of wheat starch deposit contacted with 0.01 wt% *Synperonic LF/CS 1000* + 0.5 wt% NaOH at 50°C and 4 l/min for 5 minutes.

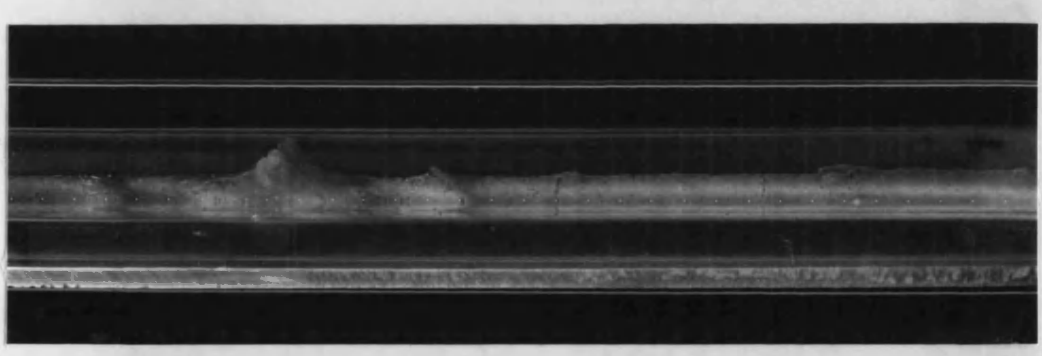


Figure 5.69(c): Photograph of wheat starch deposit contacted with 0.01 wt% *Synperonic LF/CS 1000* + 0.5 wt% NaOH at 50°C and 4 l/min for 10 minutes.

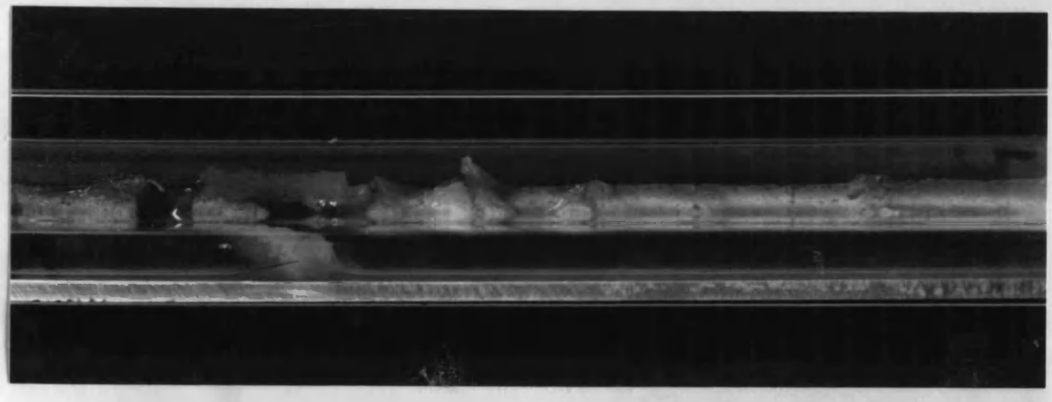


Figure 5.69(d): Photograph of wheat starch deposit contacted with 0.01 wt% *Synperonic LF/CS 1000* + 0.5 wt% NaOH at 50°C and 4 l/min for 15 minutes.

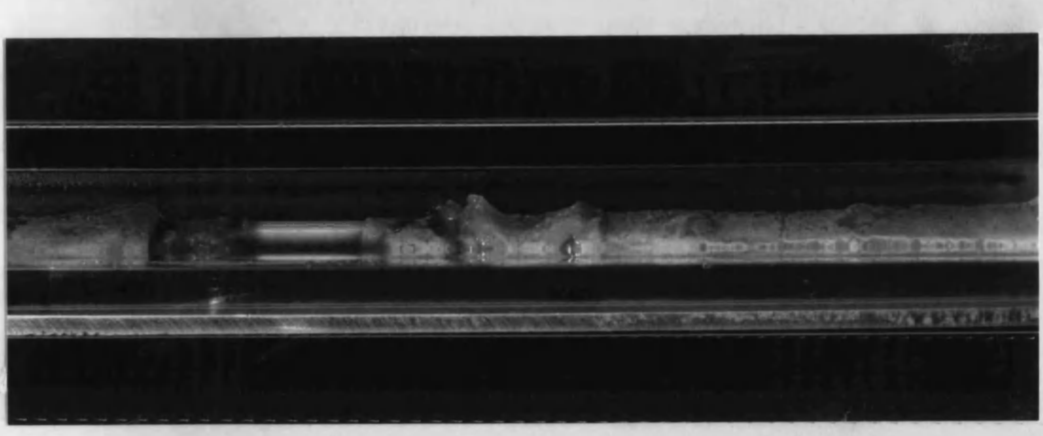


Figure 5.69(e): Photograph of wheat starch deposit contacted with 0.01 wt% *Synperonic LF/CS 1000* + 0.5 wt% NaOH at 50°C and 4 l/min for 20 minutes.

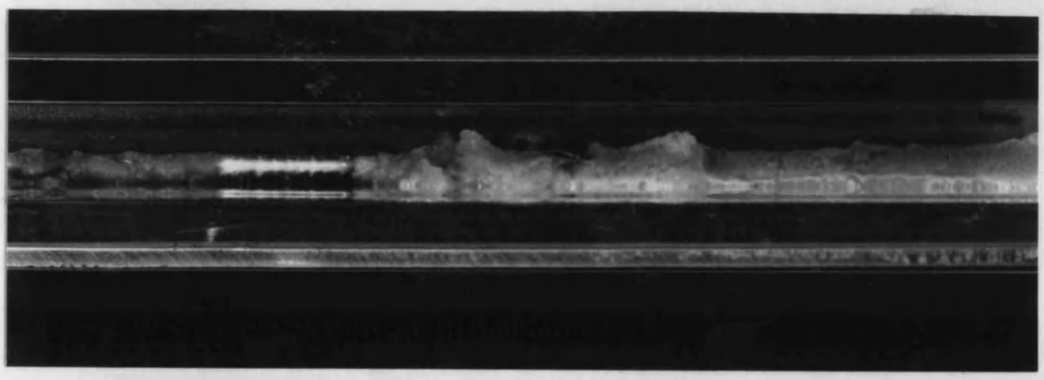


Figure 5.69(f): Photograph of wheat starch deposit contacted with 0.01 wt% *Synperonic LF/CS 1000* + 0.5 wt% NaOH at 50°C and 4 l/min for 25 minutes.

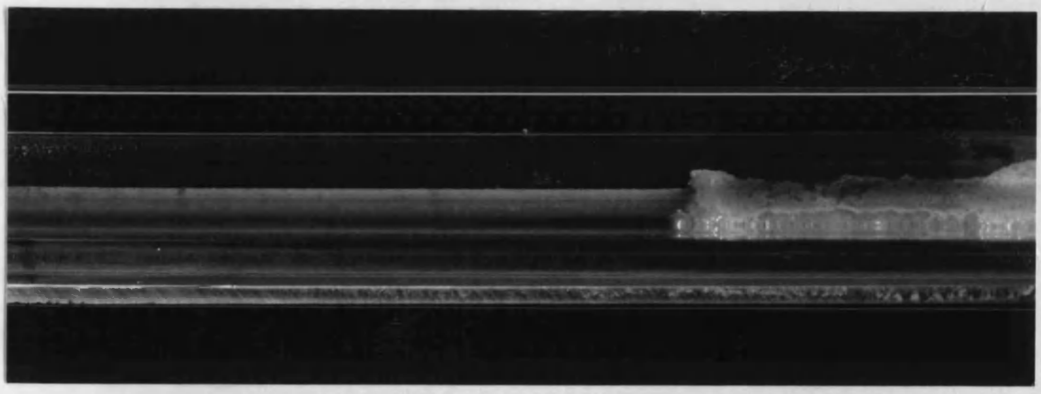


Figure 5.69(g): Photograph of wheat starch deposit contacted with 0.01 wt% *Synperonic LF/CS 1000* + 0.5 wt% NaOH at 50°C and 4 l/min for 30 minutes.

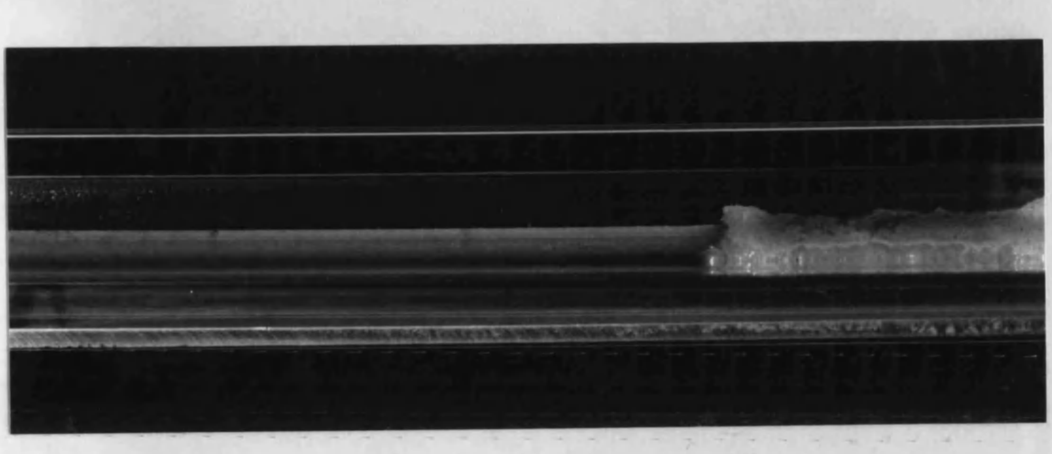


Figure 5.69(h): Photograph of wheat starch deposit contacted with 0.01 wt% *Synperonic LF/CS 1000* + 0.5 wt% NaOH at 50°C and 4 l/min for 35 minutes.

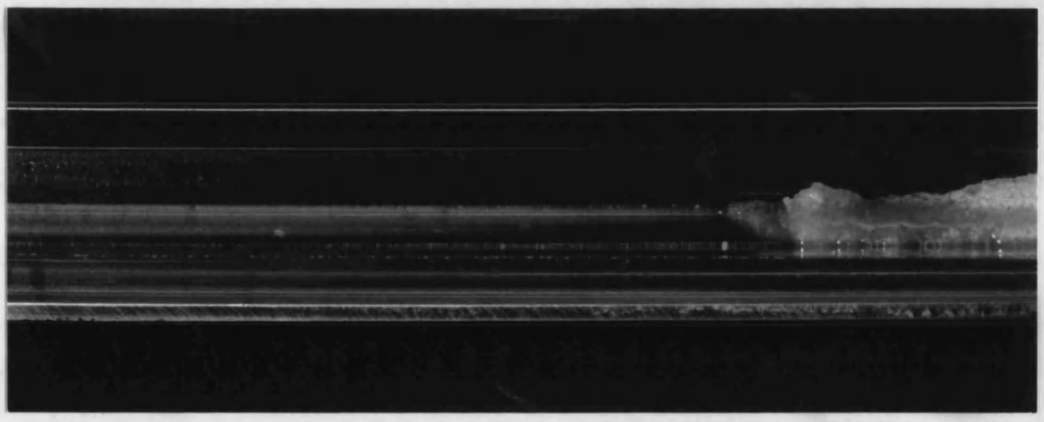


Figure 5.69(i): Photograph of wheat starch deposit contacted with 0.01 wt% *Synperonic LF/CS 1000* + 0.5 wt% NaOH at 50°C and 4 l/min for 50 minutes.

5.17.2.3 5 wt% *nitric acid at 70°C*

The effect of 5 wt% nitric acid solution was investigated at 70°C and a flow-rate of 4 l/min over a 25 minute duration (Figures 5.70(a)-(e)).

The direction of flow is from left to right. As the cleaning progresses it is clear that the removal is non-uniform: initially the deposit swells indicating a reduction in the strength of the soil-soil bonds (Figure 5.70(b)), before removal occurs by aggregate lift-off from the test-plate channel. In addition, the colour of the deposit changes on contact with the nitric acid suggesting a chemical reaction is occurring at the interface.

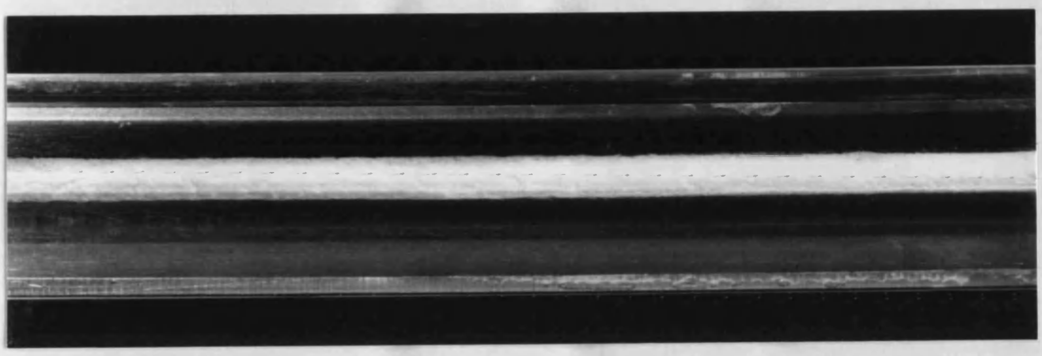


Figure 5.70(a): Photograph of wheat starch deposit contacted with 5 wt% nitric acid at 70°C and 4 l/min for 5 minutes.

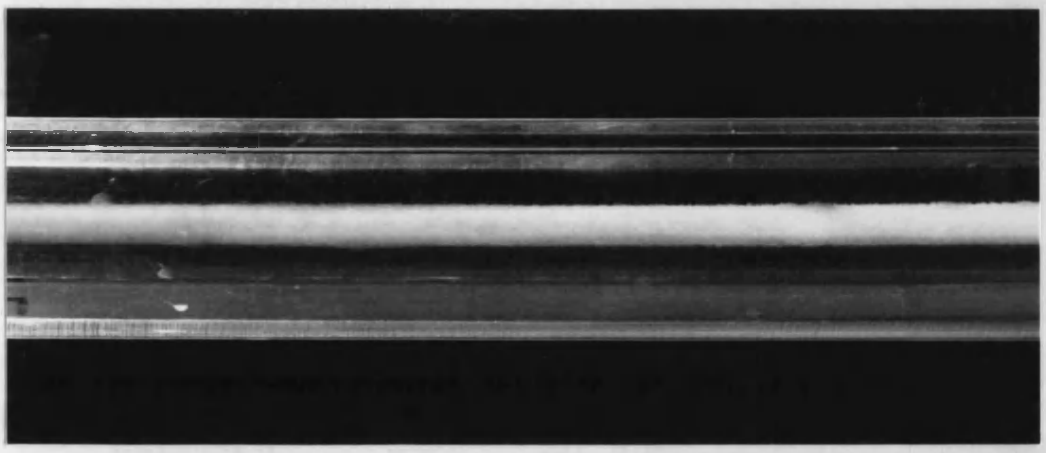


Figure 5.70(b): Photograph of wheat starch deposit contacted with 5 wt% nitric acid at 70°C and 4 l/min for 10 minutes.

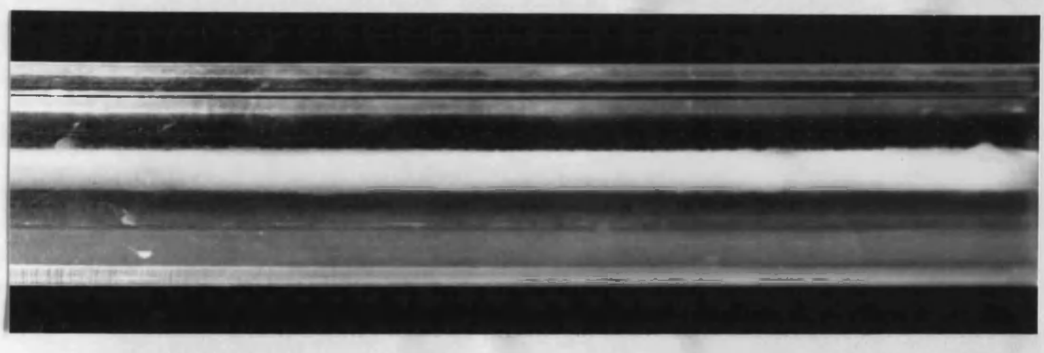


Figure 5.70(c): Photograph of wheat starch deposit contacted with 5 wt% nitric acid at 70°C and 4 l/min for 15 minutes.

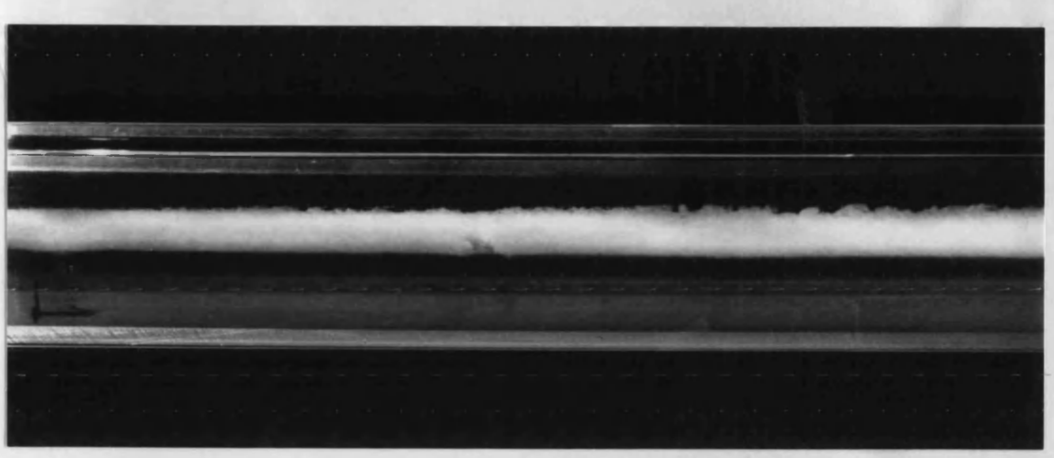


Figure 5.70(d): Photograph of wheat starch deposit contacted with 5 wt% nitric acid at 70°C and 4 l/min for 20 minutes.

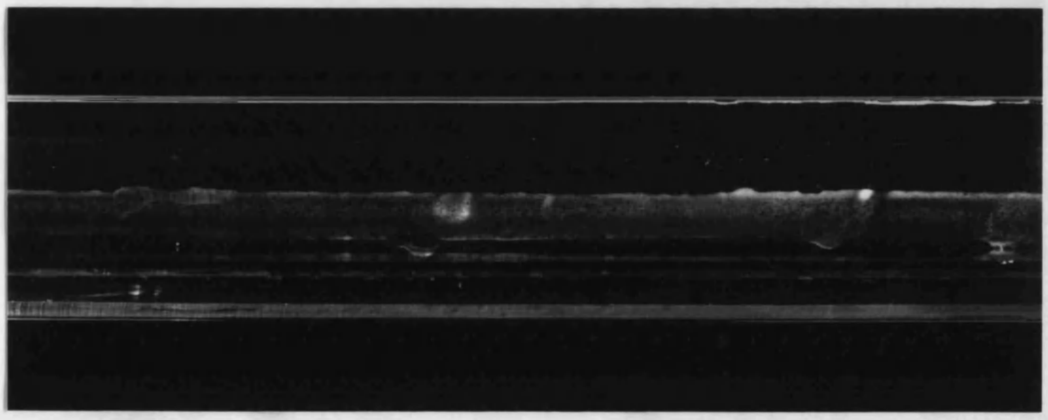


Figure 5.70(e): Photograph of wheat starch deposit contacted with 5 wt% nitric acid at 70°C and 4 l/min for 25 minutes.

5.17.2.4 0.1 wt% *thermophilic α–amylase (*Optiamyl*) at 65°C (pH=7)*

A photographic study was carried out for a deposit contacted with 0.1 wt% thermophilic α-amylase (*Optiamyl*) at 65°C (pH=7) for 25 minutes at 4 l/min. These conditions were isolated as the optimum conditions (Section 5.12). Sample photographs are given in Figures 5.71(a)-(c).

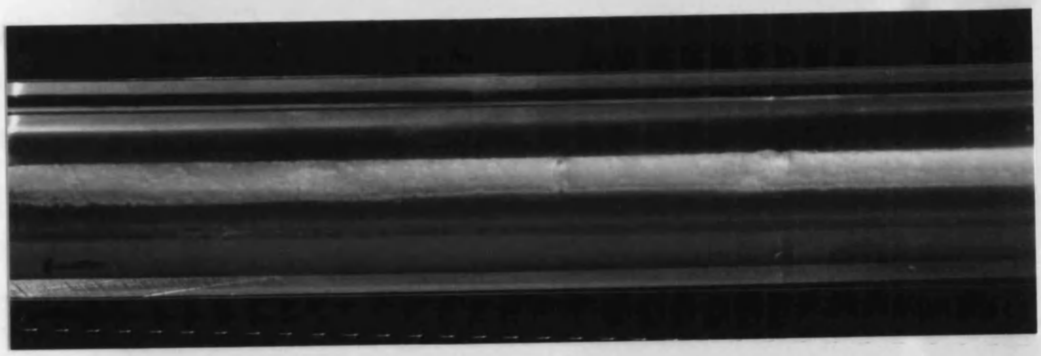


Figure 5.71(a): Photograph of wheat starch deposit contacted with 0.1 wt% thermophilic α-amylase (*Optiamyl*) at 65°C (pH=7) for 5 minutes at 4 l/min.

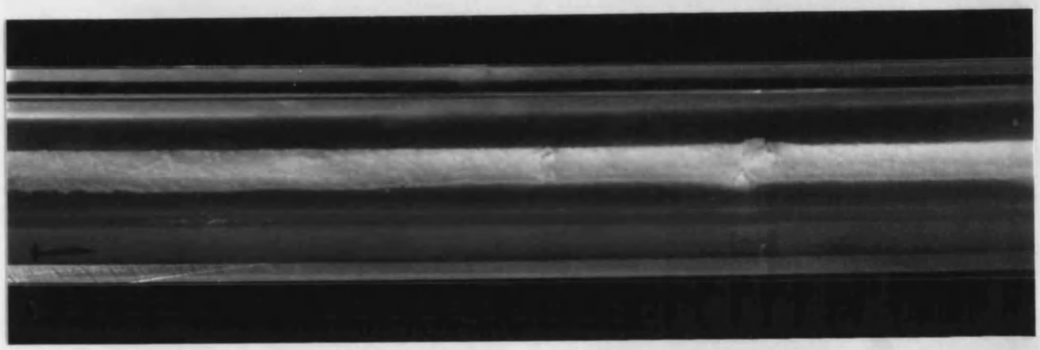


Figure 5.71(b): Photograph of wheat starch deposit contacted with 0.1 wt% thermophilic α-amylase (*Optiamyl*) at 65°C (pH=7) for 15 minutes at 4 l/min.

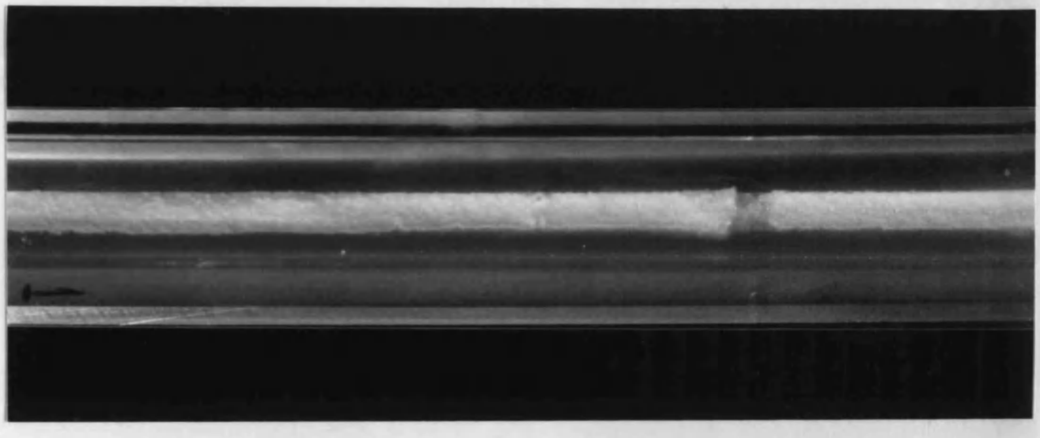


Figure 5.71(c): Photograph of wheat starch deposit contacted with 0.1 wt% thermophilic α-amylase (*Optiamyl*) at 65°C (pH=7) for 25 minutes at 4 l/min.

5.17.3 Summary

The process visualisation experiments provide an important link into the mechanisms involved in the cleaning process. It is clear that different removal patterns are observed for the various cleaners and this cleaning process is inherently non-uniform. Deposit swelling prior to removal by fluid shear in aggregate form is common to the majority of cleaners studied.

SEM studies have shown that the deposit morphology changes significantly on contact with the cleaners studied: it changes from a tightly packed low voidage form to a hollow, open structure which is susceptible to fluid shear. It is apparent that this deposit morphology is related to the overall cleaning efficiency observed: under optimum conditions the structure possesses highest voidage and is thus most susceptible to fluid shear.

Chapter 6: Modelling Starch Deposit Removal

6.1 INTRODUCTION

It was shown in the previous chapter, that the removal of starch deposits from a stainless steel surface is a complex process which exhibits different behaviour dependent on the cleaning agent applied. However, the modelling of such a system could be applied in order to optimise CIP processing in the food industry.

A literature review and discussion of modelling processes has been presented in Chapter 3. This study emphasises the importance of the energy phenomena involved in soiling and cleaning processes. Jennings [1965], was the first specialist in the food and agricultural industry to understand this aspect of the problem and he concluded that the cleanliness of a surface is a non-natural state and that soiling is a spontaneous phenomenon corresponding to a decrease in the free energy of the system. Cleaning therefore requires an energy supply large enough to cut the substrate-soil bond. In the following sections, cleaning models are developed as a direct result of the experiments described in Chapter 5.

6.2 MODELLING APPROACH

The literature study in Chapter 3 has shown that no models have been developed to describe the cleaning kinetics of baked starch deposits from hard surfaces. In order to obtain such a model for this cleaning process, a model-building procedure is followed as summarised in Table 6.1.

STAGE	DESCRIPTIVE NAME	OBJECTIVE
I	Screening variables	Determination of the significant parameters which affect the process
II	Empirical model-building	Determination of an empirical model describing the process behaviour using a mathematical expression to describe the effect of the significant parameters on the response based on the findings of Stage I

Table 6.1 Model-building procedure.

In *Stage I* of this modelling procedure, the significant parameters affecting the cleaning process have been identified i.e. temperature, concentration and flow-rate of cleaning fluid. These parameters are then applied in Stage II of this model-building procedure.

In *Stage II* empirical models are derived using a statistical analysis method based on the experimental data presented in the previous chapter for the cleaning efficiency. The models obtained will provide information about the interactive effects of the thermodynamic variables for the respective observed conditions. These models are then compared to the results obtained by intermediate parameter conditions to determine whether a good fit is obtained.

6.2.1 Experimental Design

The methodology of multiple linear regression was applied to the experimental design and used to model the cleaning behaviour observed for the alcohol ethoxylate, $C_{9-11}E_6$ (*Stage I*). The general expression for this is defined for more than one factor (x) as:

$$y = b_0 + b_1x_1 + b_2x_2 + ... + b_ix_i \qquad (b_i - \text{coefficient for } x_i) \qquad (6.1)$$

For this purpose, the measured cleaning efficiency after a 25 minutes duration (expressed as a percentage) was applied to run a series of DOX experiments in order to study the influence of the operating parameters on the cleaning efficiency.

There were three main goals for applying multiple linear regression:

1. Determine which factors were most significant and which factor coefficients were statistically non-zero.
2. Create a mathematical equation that best captured the knowledge on the system by including the significant factors in the model.
3. Determine if the model accurately predicted the results i.e. how did the predicted value for the result compare to the actual observed value.

To study the influence of the three operating parameters on the cleaning efficiency, 16 experimental runs were carried out. Suitable coding of the operating parameters results in the experimental design matrix described in Table 6.1.

The independent variables in this table were coded according to:

CODED	-1	0	1
UNCODED	x_{low}	x_{mid}	x_{high}

$$x_{coded} = \frac{2x_{uncoded} - x_{high} - x_{low}}{x_{high} - x_{low}} \qquad (6.2)$$

The operating variables are namely the concentration, temperature and flowrate of the $C_{9\text{-}11}E_6$. Important calculated parameters used in the DOX analysis are R-square and RMSE (Root Mean Square Error) terms. An indication on the fit of the model can be indicated by the R^2 term which describes the ratio of the variability in the response (y) explained by the model (Regression SS) to the total variability of the response (Total SS). This term will be the largest when all the terms in the model are included, regardless of whether the terms are statistically significant. However, it will decrease slightly when non significant terms dropped from the model and decreases greatly when significant terms are dropped incorrectly (i.e. acts as a sensitivity indicator to variables).

$$R^2 = \frac{\text{Regression SS}}{\text{Total SS}} \text{x } 100$$

CONC (wt%)	TEMPERATURE (°C)	FLOW (l/min)
0-4	25-70	1-6
4-10	25-70	1-6
10-15	25-70	1-6

Table 6.2: Ranges of operating parameters studied for $C_{9\text{-}11}E_6$ in three factor factorial design using multiple linear regression.

The Root Mean Square Error (RMSE) is defined as:

$$\text{RMSE} = \left(\frac{\text{sum of (residuals}^2)}{\text{no. of exp} - \text{no. of terms in model}} \right)^{1/2}$$

RMSE is the standard error for the predicted values and is the measure of how well the model fits the data. This term decreases when insignificant coefficients are dropped incorrectly and is a minimum when correct terms are used in the model.

Figure 6.1 summarises in flowsheet form the methodology adopted in modelling and analysing the results for the cleaning of $C_{9\text{-}11}E_6$.

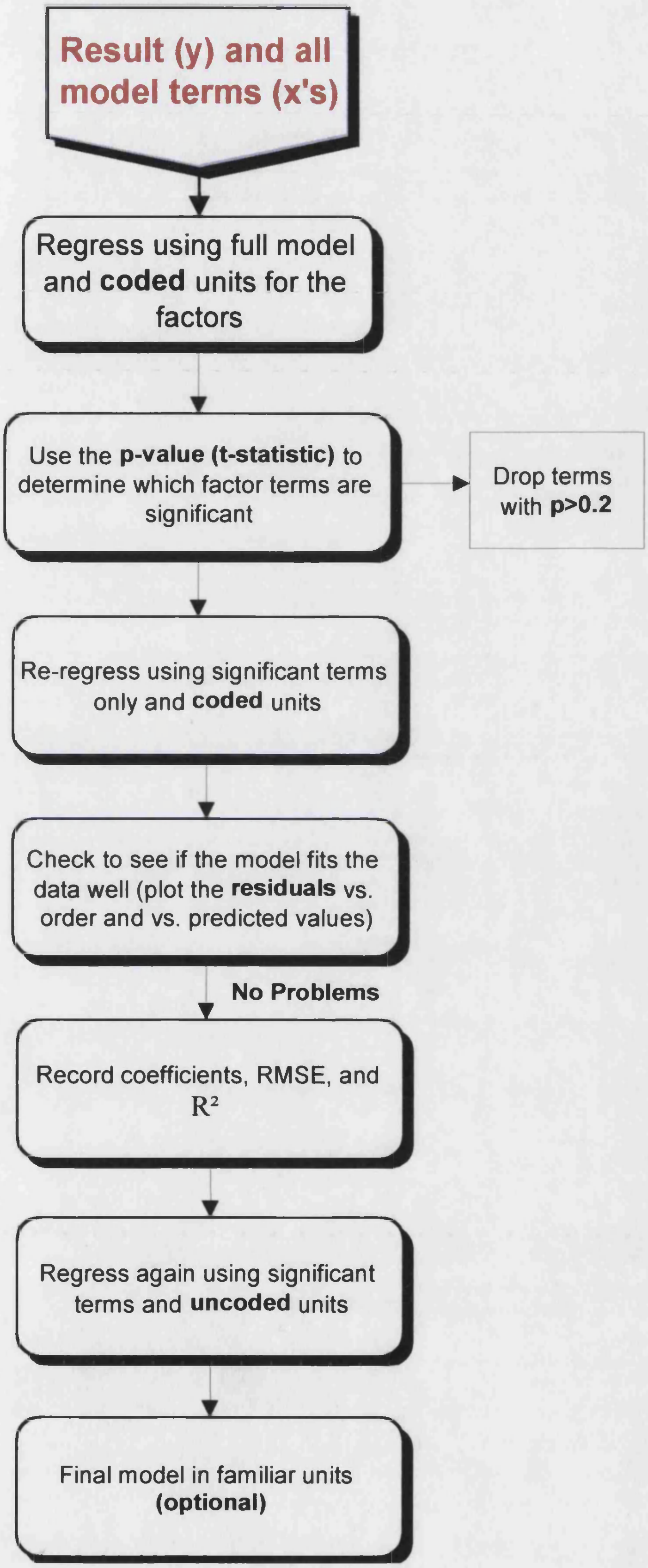


Figure 6.1 Methodology for application to multiple linear regression of DOX experiments.

6.2.2 Regression Results

The following equations were derived using the regression macro tool and the data analysis macro outputs are included in Appendix A2.

CONC (wt%)	TEMP (°C)	FLOW (l/min)	REGRESSION EQUATION	RMSE	R^2
0-4	25-70	1-6	$y = 11.80 + 10.20C + 0.6F + 1.59CF$	11.38	98.68
0-10	25-70	1-6	$y = 5.8 + 0.77C + 1.60F + 0.78CF$	14.88	96.47
0-15	25-70	1-6	$y = 5.8 + 1.23C + 1.60F + 0.48CF$	5.02	99.59

Table 6.3: Linear regression equations (uncoded) and statistical data derived for the ranges of operating parameters studied for $C_{9-11}E_6$ in a three factor factorial design (see Appendix A2).

6.2.3 Discussion of Regression Analysis

The discussion of the operating parameters influencing the cleaning efficiency observed using the results of the linear regression model are discussed with reference to the relative concentrations of $C_{9-11}E_6$ used.

6.2.3.1 *Concentration Range 0-4wt%* $C_{9-11}E_6$

The Pareto charts depict the relative interactive effects are observed for the temperature band 25-70°C over this concentration range. The intercept, (constant b_o), indicates the standardised cleaning efficiency constant and was obtained from the coded values of the regression being transposed into uncoded format (in order to represent real values), prior to repeating the regression analysis and thus obtaining the derived equations.

The greatest influencing factor is the concentration, followed by the interaction of the flow-rate and concentration parameters and then of the flow-rate alone. This information can also be seen from the standardised effects given in the Pareto diagram (Figure 6.2). The positive sign of the first-order coefficients in the equations of Table 6.3 for the concentration terms, indicate that within this experimental range any increase in the concentration above the reference conditions results in an increase of the cleaning efficiency.

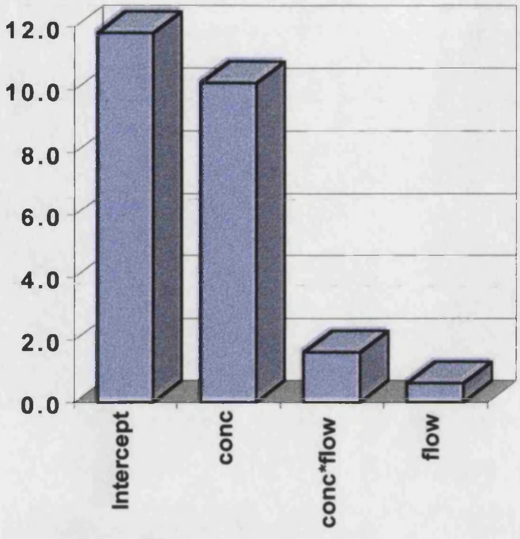


Figure 6.2: Pareto chart of standardised effects of the linear regression on 0-4wt% $C_{9\text{-}11}E_6$ in cleaning between 25 to 70°C at a flowrate range of 1-6 l/min: $y = 11.80 + 10.20C + 0.6F + 1.59CF$

6.2.3.2 *Concentration Range 0-10wt%* $C_{9\text{-}11}E_6$

The positive coefficient of the constant b_o indicates the cleaning efficiency is enhanced at these reference conditions (Figure 6.3)

In contrast to the model proposed for the 0-4wt% concentration range, the greatest influencing factor is the flow, followed by the second order interaction of concentration and flow and then concentration alone. It is likely that the increased shear stresses created by the greater flowrate contributes to the improvement in the cleaning efficiency observed in tandem to the fact that an optimum concentration may have been achieved (Chapter 5).

A good fit for the data is indicated by the value of the R^2 term (96.47%).

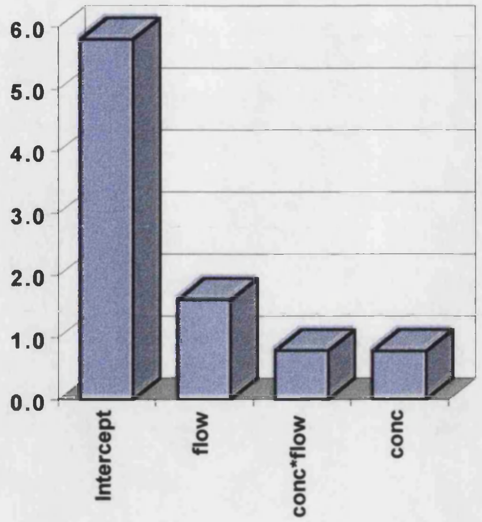


Figure 6.3: Pareto chart of standardised effects of the linear regression on 0-10wt% $C_{9\text{-}11}E_6$ in cleaning between 25 to 70°C at a flowrate range of 1-6 l/min: $y = 5.8 + 0.77C + 1.60F + 0.78CF$

6.2.3.2 *Concentration Range 0-15wt%* $C_{9\text{-}11}E_6$

The positive coefficient of the constant b_o indicates the cleaning efficiency is enhanced at these reference conditions (Figure 6.4)

The greatest influencing factor is the flow, followed by the concentration and then the interaction of concentration and flow. It is likely that the increased shear stresses created by the greater flowrate contributes to the improvement in the cleaning efficiency observed as was observed in the previous case.

A good fit for the data is indicated by the value of the R^2 term (99.59%). Table 6.4 depicts the data matrix using the *Statman* macro tool under these conditions.

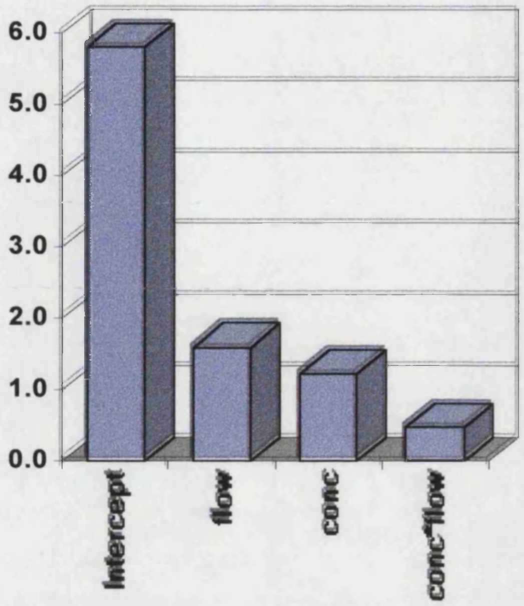


Figure 6.4: Pareto chart of standardised effects of the linear regression on 0-15wt% $C_{9\text{-}11}E_6$ in cleaning between 25 to 70°C at a flowrate range of 1-6 l/min: $y = 5.8 + 1.23C + 1.60F + 0.48CF$

Run	CONC	TEMP	FLOW	Actual	Predicted
1	0	70	6	16.5	18.3
2	0	25	1	6.2	8.0
3	0	70	1	8.6	6.8
4	15	25	6	66	67.8
5	15	70	6	88	86.2
6	0	25	6	14.3	12.5
7	15	25	1	29	27.2
8	15	70	1	37	38.8

Table 6.4: Data matrix obtained using a linear regression (*Statman* macro) tool to obtain predicted cleaning efficiency on 0-15wt% $C_{9\text{-}11}E_6$ between 25 to 70°C at a flowrate range of 1-6 l/min

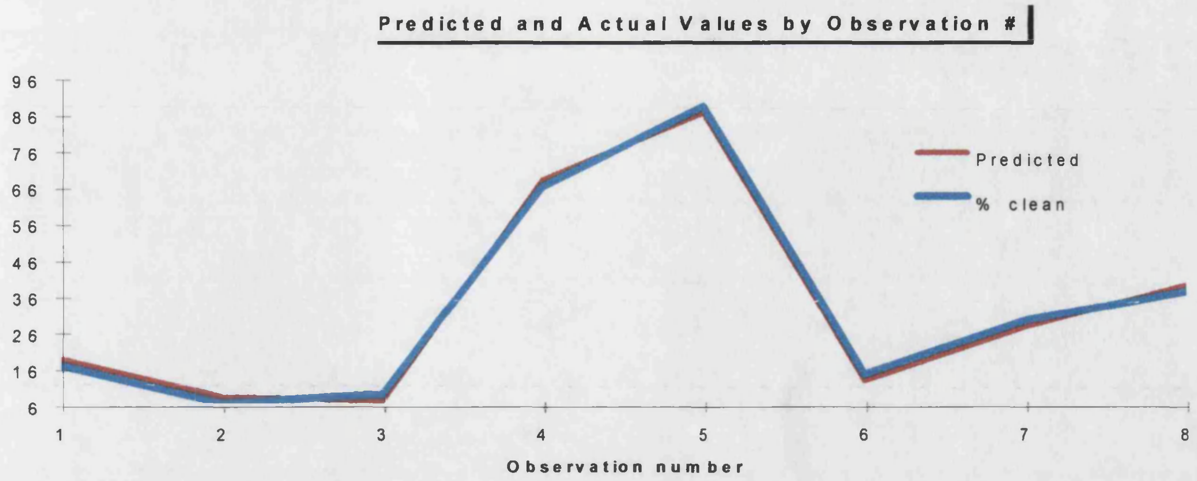


Figure 6.5: Plot of predicted cleaning efficiency using linear regression equation: $y = 5.8 + 1.23C + 1.60F + 0.48CF$ versus observed cleaning efficiency on 0-15wt% $C_{9\text{-}11}E_6$ between 25 to 70°C for a flowrate range of 1-6 l/min.

6.2.4 Comparison of Models to Experimental Results

The three models determined are verified in this section by comparing the actual cleaning efficiencies observed for experiments that are conducted independently at intermediate conditions. This data is obtained from the intermediate condition experimental conditions described in Chapter 5 and is depicted in Table 6.5 and Figure 6.6.

Observation #	*CONC (C)*	*FLOW (F)*	*TEMP (T)*	*Model*	*Actual*
1	3	1	25	47.77	23.8
2	3	1	70	47.77	36.5
3	3	6	25	74.62	61.3
4	3	6	70	74.62	72.6
5	5	1	25	15.15	16.9
6	5	1	70	15.15	31.3
7	5	6	25	42.65	56.1
8	5	6	70	42.65	89.4
9	12	1	25	27.92	11.2
10	12	1	70	27.92	21.1
11	12	6	25	64.72	58.1
12	12	6	70	64.72	77.6

Table 6.5: A comparison of data obtained by experiment versus that obtained using the derived model equations using intermediate concentration conditions.

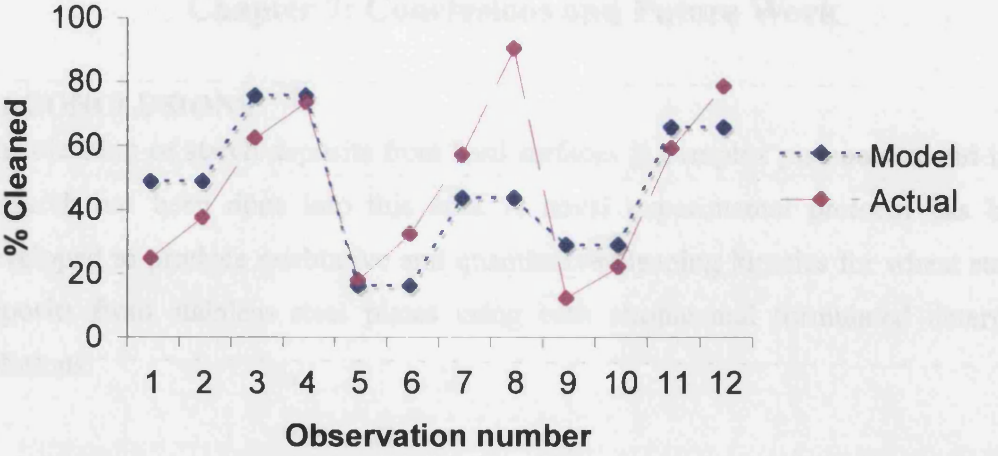


Figure 6.6: Plot of predicted cleaning efficiency using derived statistical models versus actual data obtained by experimental runs for intermediate concentration conditions

6.3 MODEL CONCLUSIONS

The statistical analysis of data has been performed using linear regression of three variables involved in the cleaning process: concentration, flowrate and temperature. In application of this methodology, response function equations were determined to describe the influence of the operating parameters on $C_{9\text{-}11}E_6$ cleaning efficiency under three ranges of concentration. The magnitude of the R-square and RMSE terms in the regression provided an indication on the confidence level associated with the equations derived from the data. The models were then tested for validity using intermediate concentration conditions and independent experimental data (described in Chapter 5). The actual results obtained and the predicted model data indicated a good correlation suggesting the models were appropriate descriptions of the removal behaviour observed under these thermohydraulic conditions. As a next step in the development of the model it is proposed that further work is done to determine whether the optimum concentration for cleaning can be predicted from the models. This may be achieved by differentiating the model equations with respect to concentration and determining the values of concentration required to obtain a maxima for the equations derived. It is also interesting to note that temperature does not appear to play a significant part in the models obtained from the statistical analysis for the thermohydraulic conditions investigated: concentration and flow are the key parameters in the removal process.

Chapter 7: Conclusions and Future Work

7.1 CONCLUSIONS

The cleaning of starch deposits from hard surfaces is complex phenomena and little research has been done into this area. A novel experimental protocol has been developed to produce qualitative and quantitative cleaning kinetics for wheat starch deposits from stainless steel plates using both simple and formulated detergent solutions.

7.1.1 Experimental Design

The study is divided into two main experimental sections: the first concerns a static cleaning study of modified potato starch deposit removal from stainless steel surfaces using an ultrasonic cleaning bath. The results indicate an optimum concentration of 14wt% for both sodium hydroxide and nitric acid. The existence of temperature optima at $60^{\circ}C$ was also found for sodium hydroxide. This corresponds to the gelatinization temperature of the potato starch which is observed by a marked increase in the degree of swelling of the deposit. The swelling effect exhibited by the soil had two effects on the detersive process. First it altered the nature of the soil surface making it more like a water surface. Secondly, it allowed diffusion of bath components to the interior of the deposit, where they are adsorbed and taken out of action or may diffuse to the substrate-soil interface and get directly into the action of breaking the soil-substrate bonds: the cleaning efficiencies are low during the initial immersion stage but rapidly increase as the potato deposit lifts off the disc. This would provide an explanation for the marked swelling with increasing temperature. The swelling phenomenon was noticed to be more pronounced in sodium hydroxide cleaning than when using nitric acid which attacks the surface without penetrating the soil and hence less swelling is observed. Harper implies that the main property of acid cleaning agents is to dissolve rather than to penetrate and emulsify the soil. An increase in the concentration of the commercial cleaner (*Micro*) at $60^{\circ}C$ did not affect the cleaning efficiency over the concentration range considered in these static experiments. The enzyme BAN (Bacterial Amylase Novo), an α-amylase, showed a strong dependence between the temperature and cleaning time, although no optimum temperature was found for the range considered. For the enzyme β-glucanase, a concentration dependency exists for the removal rate of deposit over the range considered, although no optimum was found.

The other, more detailed investigation involves the study of the cleaning of baked wheat starch deposits from stainless steel surfaces under controlled thermo-hydraulic conditions.

The effects of temperature and concentration of a variety of cleaning agents were studied in pilot ultrasonic cleaning experiments using baked potato starch. Many aspects of this study were subsequently applied to cleaning study of baked wheat starch deposits from stainless steel surfaces under controlled thermo-hydraulic conditions.

The experimental system consisted of two rigs:

Fouling rig: Used to generate uniformly fouled stainless steel plates.

Cleaning rig: Used to clean the fouled plates under controlled conditions of concentration, temperature and flow-rate.

A quantitative analysis of the removal process was obtained using a gravimetric method: weighing the fouled test plates before and after cleaning. A qualitative analysis was performed by direct visualisation using high-speed video photography (without optical distortion by the use of a rectangular cross-sectional glass cell).

7.1.2 Experimental Results

Experiments were performed to examine both the mechanistic processes involved in soil removal and the effect of process variables and cleaning formulations upon the cleaning kinetics.

The most effective detergent studied was the non-ionic surfactant $C_{9\text{-}11}E_6$ and hence was studied in more detail. In addition the deposit removal kinetics were strongly affected by the cleaning solution temperature, concentration and flow-rate.

The results of the cleaning tests can be related to the physical properties of the starches. The cleaning solution temperature required is comparable to the degree of swelling of the deposit and the mean gelatinization temperature. At higher swelling levels the bindings within the deposit become weaker and more susceptible to thermal and mechanical influences. The higher resistance of the wheat starch residues may be attributed to the increased strength of phosphate linked starches due to thermal and mechanical treatments.

It was observed that the non-ionic surfactant was most effective when used up to 10°C below and 20°C above its cloud point temperature. This relates to the segregation of the surfactant into two distinct phases; one rich in water and the other rich in surfactant. The best cleaning efficiencies were observed for concentrations of surfactant well above the cmc. At these concentrations, it is believed that the polar groups are sufficiently hydrated to form a viscous interface-modifying film structured by lateral hydrogen bonding via intermediate water molecules.

It has been determined that optimum cleaning solution concentrations exist which are related to the deposit voidage structures observed using an SEM study. Hence the selection of the optimum cleaning solution concentration is of paramount importance when designing CIP cycles.

The influence of cleaning solution flow-rate and hence Reynolds number, also has a favourable effect upon the time required to clean due to the greater shear stress effects created. This influence was aided by the swelling phenomena of the deposit created by certain cleaning solutions due to their wetting influences.

7.1.3 Mathematical Modelling

Modelling of the cleaning process was developed from the data of a series of DOX experiments and the statistical analysis using linear regression of the variables involved. Hence, response function equations were obtained to describe the influence of the operating parameters on $C_{9\text{-}11}E_6$ cleaning efficiency.

The magnitude of the R-square and RMSE terms in the regression provided an indication on the confidence level associated with the equations derived from the data. The models were then tested for validity using intermediate concentration conditions and independent experimental data (described in Chapter 5). The actual results obtained and the predicted model data indicated a good correlation suggesting the models were appropriate descriptions of the removal behaviour observed under the tested thermohydraulic conditions. As a next step in the development of the model it is proposed to determine whether the optimum concentration for cleaning can be predicted from the models described. This may be achieved by differentiating the model equations with respect to concentration and determining the values of concentration required to obtain a maxima for the equations derived. It is also interesting to note that temperature does not appear to play a significant part in the models obtained from the statistical analysis for the thermohydraulic conditions investigated: concentration and flow are the key parameters in the removal process.

7.2 FUTURE WORK

The apparatus developed for the study of baked wheat starch deposit removal from stainless steel surfaces has opened a variety of opportunities for future work. In the following sections the development of many aspects of the work described in this report is considered.

7.2.1 Fouling Process

The mechanisms involved in the formation of the fouled wheat deposit would be of industrial benefit in order to design equipment to resist deposition. The processes involved in the fouling process are complex and their theory is discussed in Chapter 2, but a detailed analysis of the fouling kinetics for this particular soil would prove beneficial. In the design of experiments, the types of fouling that may occur must be considered. It is envisaged that two mechanisms for starch deposit formation onto a conditioned surface may need to be considered:

1. **Reaction on the heat transfer surface**: fouling is controlled by a heterogeneous reaction between the starch and the heat transfer surface, giving aggregation on the surface.
2. **Thermal boundary layer fouling**: fouling is controlled by homogeneous reaction in the fluid, but only the thermal boundary layer next to the heat transfer surface is hot enough for aggregation to take place.

A useful technique to observe temperature variations during the fouling process could be provided by the use of a thermal imaging techniques.

A more detailed study of the influence of relative constituents to the wheat flour substrate would provide useful information on the adhesion properties.

Although stainless steel has been used as the substrate for the test-plates and a homogeneous surface roughness adopted, it is believed that adhesion properties should be studied for other materials and the influence of varying surface roughness be investigated in further detail.

7.2.2 Cleaning Process

7.2.2.1 *Detergent composition*

The cleaning protocol developed could be used to investigate the effects of different cleaning agent compositions and their interactions. In particular, the synergy between components and their overall impact on cleaning efficiency; in a similar manner to the addition of EDTA and *Synperonic LF/CS 1000* to sodium hydroxide. The impact and kinetics of rinsing after using cleaning solutions provides a wide scope for study. This process is principally a fluid mechanical phenomenon but is a prerequisite to a complete CIP cycle optimisation.

7.2.2.2 *Biochemical Effects*

Although this study has principally been directed with an engineering bias, a detailed examination of the biochemistry of starch deposit interaction with cleaning agents to provide explanations for the structural changes to the matrix has not been undertaken. A further step to this work could involve a quantification of the swelling observed using a kinetic study.

7.2.2.3 *Optimising cleaning conditions*

This study has identified the existence of cleaning conditions based on the variables of temperature, concentration and flow-rate which could be applied in the design of a CIP cycle. This optimisation could lead to a significant economic impact in terms of cost reduction in terms of time and quantities of materials used. Hence it is important to reapply the learnings from this study to isolate the optimal cleaning conditions over a wide range of starch soil applications in the food industry. Hence results should be confirmed for a wide range of fouling and cleaning conditions applied in an industrial environment.

7.2.2.4 *Cleaning non-starch based soils using thermal processing*

The rig designed is versatile and has the capability to study a number of food soils besides starch based products. Such studies would need a similar validation protocol to be adopted as in this study to understand the fouling and cleaning mechanisms involved.

7.2.2.5 *Pulsatile flow*

In circulation cleaning and spray cleaning, the friction between deposited soil and fluid past it provides the energy source essential for final displacement of the soil deposit. The shear force so generated is related to turbulence of the solution. This effect can be enhanced by the use of pulsatile flow. A small alteration to the design of the cleaning rig would enable the study of such effects for starch deposits. In addition the cleaning efficiencies observed for entrained air within the system could be studied to determine whether increased scrubbing action or turbulence due to slugs of air has an effect. Again, the optimal design and operation of such cleaning cycles could aid industry in CIP processing.

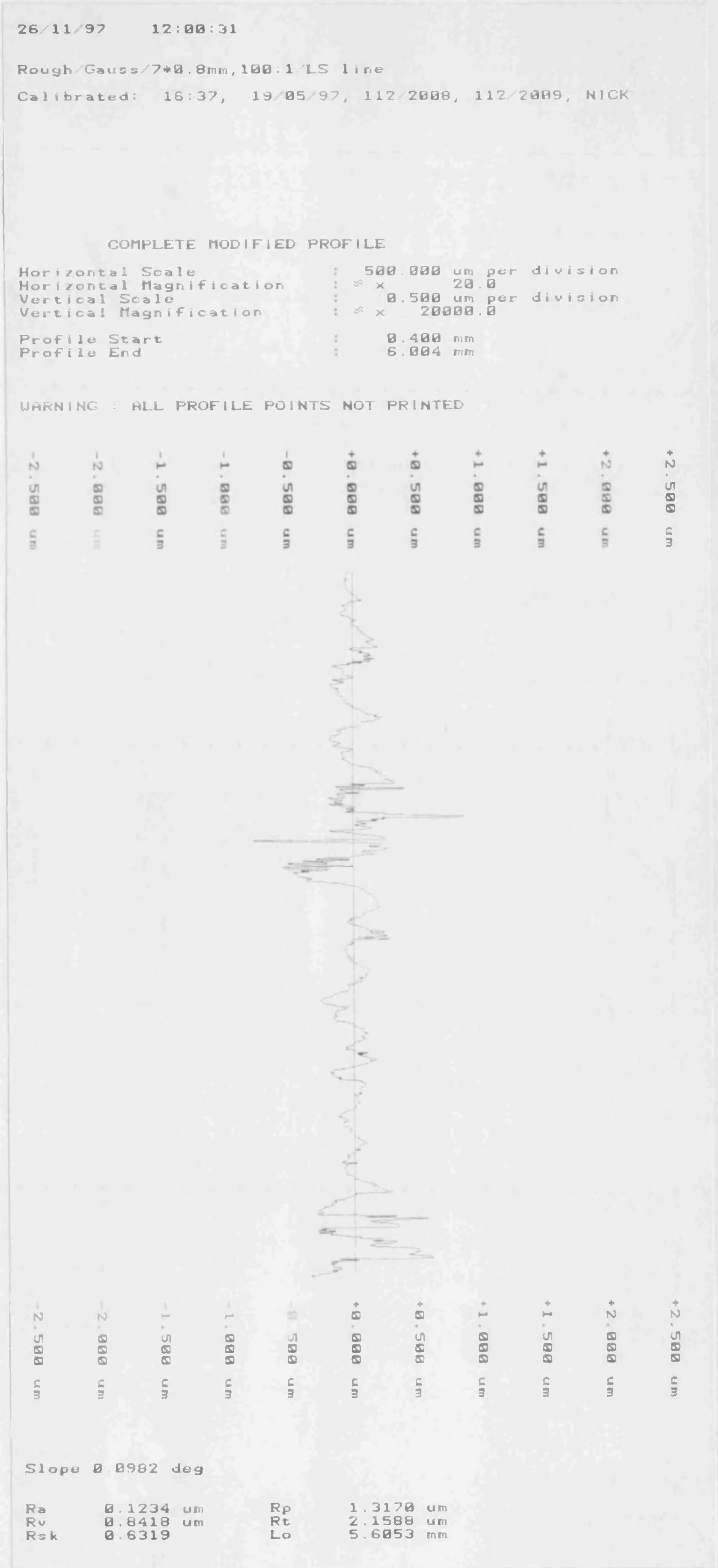
APPENDIX A1
SURFACE ROUGHNESS

The measurement and characterisation of surface finishes is of such complexity that it may be considered a science in its own right.

Surface roughness is defined by Romney [1990] as the fine disturbances which constitute the main surface pattern. It is of interest in cleaning studies since the magnitude of the soil-substrate bond is usually stronger than the soil-soil bond. The surface roughness can be characterised by several parameters derived from the amplitude measurements made of a sample length: R_a is the most commonly used international parameter of surface roughness. The R_a value corresponds to the arithmetic mean of the departures of the roughness profile from the centre line

Measurements were made of the stainless test pieces used in the fouling and cleaning experiments using a Rank Taylor Hobson form Talysurf surface roughness machine The test plates used were 316 stainless steel and buffed with 320G grade paper during manufacture.

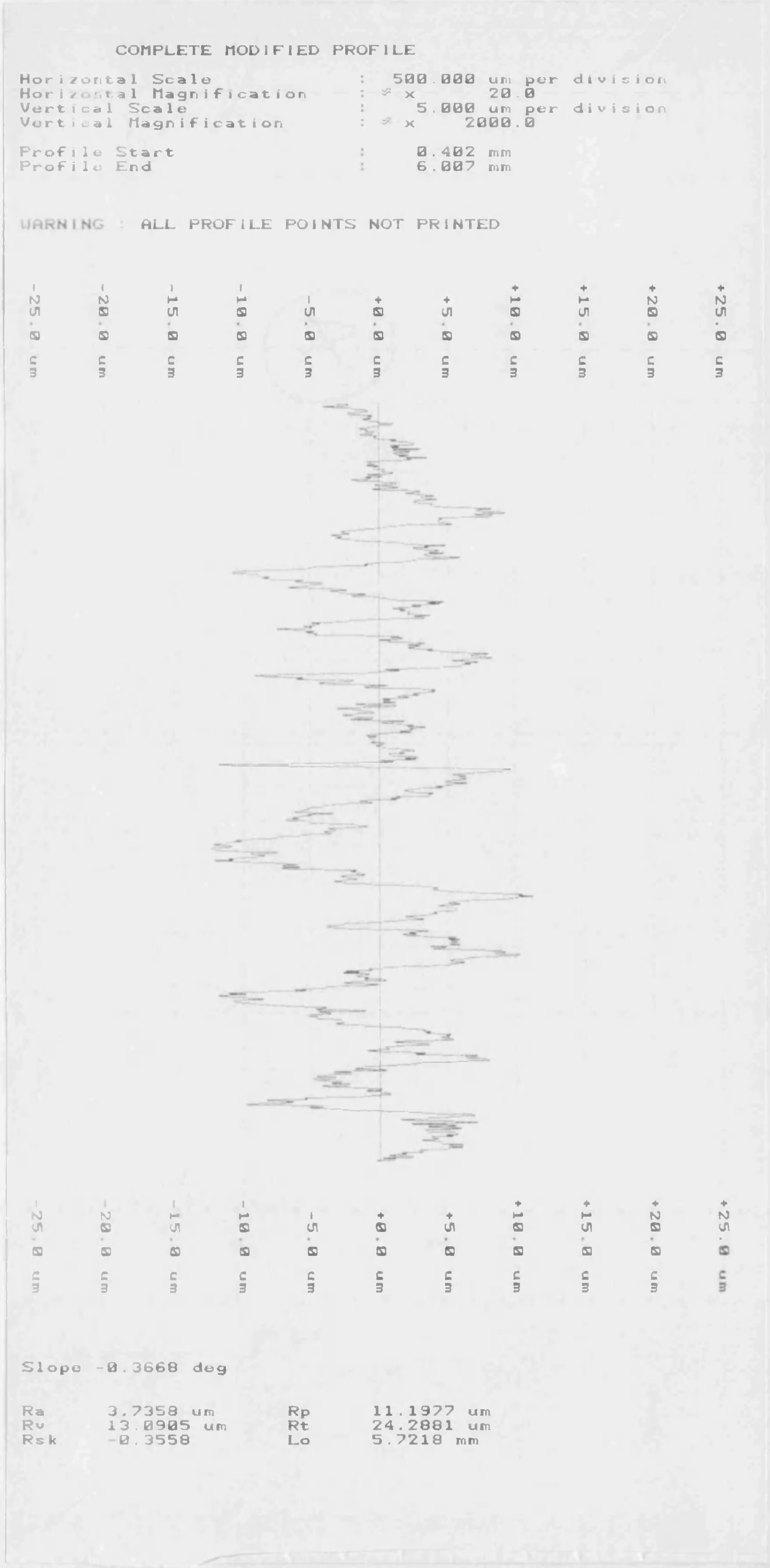
The surface roughness machine was comprised of a fine stylus, (diameter 1μm), which travelled over a sample distance of 6mm (arbitrarily chosen). Measurements were taken over 5 runs and the results averaged (R_a= 0.009mm). The roughness values are discussed on p60 and a sample profile is depicted in Figure A1.1. The measurements were repeated using fouled test-plate samples and the results again averaged over 5 runs (R_a= 3.399mm) and a sample profile is depicted in Figure A1.2. A good correlation between R_a values is achieved in each case indicating a good reproducibility of data between measurements.



```
26/11/97      12:00:31

Rough/Gauss/7*0.8mm,100:1/LS line

Calibrated:  16:37,  19/05/97, 112/2008, 112/2009, NICK




        COMPLETE MODIFIED PROFILE

Horizontal Scale                :  500.000 um per division
Horizontal Magnification        : ≈ x       20.0
Vertical Scale                  :    0.500 um per division
Vertical Magnification          : ≈ x   20000.0

Profile Start                   :    0.400 mm
Profile End                     :    6.004 mm


WARNING : ALL PROFILE POINTS NOT PRINTED
```

```
Slope 0.0982 deg

Ra      0.1234 um        Rp      1.3170 um
Rv      0.8418 um        Rt      2.1588 um
Rsk     0.6319           Lo      5.6053 mm
```

Figure A1.1 Sample Talysurf profiles from stainless steel test-plates



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        COMPLETE MODIFIED PROFILE

Horizontal Scale                : 500.000 um per division
Horizontal Magnification        :  x        20.0
Vertical Scale                  :    5.000 um per division
Vertical Magnification          :  x     2000.0

Profile Start                   :    0.402 mm
Profile End                     :    6.007 mm


WARNING : ALL PROFILE POINTS NOT PRINTED
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```
Slope -0.3668 deg

Ra       3.7358 um          Rp        11.1977 um
Rv       13.0905 um         Rt        24.2881 um
Rsk      -0.3558            Lo        5.7218 mm
```

Figure A1.2 Sample Talysurf profiles from stainless steel test-plates

3 Factor Factorial Design for 0-4wt% Ethoxy

NAME	conc	temp	flow
HIGH	4	70	6
LOW	0	25	1

Run	conc	temp	flow	% clean
1	0	70	6	16.5
2	0	25	1	16.2
3	0	70	1	8.6
4	4	25	6	88.7
5	4	70	6	99.8
6	0	25	6	14.3
7	4	25	1	42.8
8	4	70	1	76.3

coded inputs for regression

conc	temp	flow	conc*temp	conc*flow	temp*flow
-1	1	1	-1	-1	1
-1	-1	-1	1	1	1
-1	1	-1	-1	1	-1
1	-1	1	-1	1	-1
1	1	1	1	1	1
-1	-1	1	1	-1	-1
1	-1	-1	-1	-1	1
1	1	-1	1	-1	-1

Regression Results for % clean (coded)

	Coefficients	Std. Dev.	t-statistic	Prob>|t|
Intercept	45.40000	4.02500	11.280	0.0563
conc	31.50000	4.02500	7.826	0.0809
temp	4.90000	4.02500	1.217	0.4378
flow	9.42500	4.02500	2.342	0.2569
conc*temp	6.25000	4.02500	1.553	0.3642
conc*flow	7.92500	4.02500	1.969	0.2992
temp*flow	-1.57500	4.02500	-0.391	0.7625

A N O V A

Source	Sum of Squares	df	Mean Square	RMSE
Regression	9675.52	6	1612.59	
Error	129.61	1	129.61	11.38
Total	9805.12			

note: p-value is for two-sided t-te

R-square	F	Prob > F
98.68%	12.44	.2137

UNCODED VALUES:

	Coefficients	Std. Dev.	t-statistic	Prob>|t|
Intercept	11.80000	10.99980	1.073	0.3438
conc	10.20250	3.88902	2.623	0.0586
flow	0.60000	2.55740	0.235	0.8260
conc*flow	1.58500	0.90418	1.753	0.1545

A N O V A

Source	Sum of Squares	df	Mean Square	RMSE
Regression	9151.09	3	3050.36	
Error	654.03	4	163.51	12.79
Total	9805.12			

note: p-value is for two-sided t-te

R-square	F	Prob > F
93.33%	18.66	.0082

3 Factor Factorial Design for 0-10wt% Ethoxy

NAME	conc	temp	flow
HIGH	10	70	6
LOW	0	25	1

Run	conc	temp	flow	% clean
1	0	70	6	16.5
2	0	25	1	6.2
3	0	70	1	8.6
4	10	25	6	43
5	10	70	6	97
6	0	25	6	14.3
7	10	25	1	16.9
8	10	70	1	29

coded inputs for regression

conc	temp	flow	conc*temp	conc*flow	temp*flow
-1	1	1	-1	-1	1
-1	-1	-1	1	1	1
-1	1	-1	-1	1	-1
1	-1	1	-1	1	-1
1	1	1	1	1	1
-1	-1	1	1	-1	-1
1	-1	-1	-1	-1	1
1	1	-1	1	-1	-1

Regression Results for % clean

	Coefficients	Std. Dev.	t-statistic	Prob>|t|
Intercept	28.93750	5.26250	5.499	0.1145
conc	17.53750	5.26250	3.333	0.1856
temp	8.83750	5.26250	1.679	0.3419
flow	13.76250	5.26250	2.615	0.2325
conc*temp	7.68750	5.26250	1.461	0.3822
conc*flow	9.76250	5.26250	1.855	0.3147
temp*flow	5.21250	5.26250	0.990	0.5030

A N O V A

Source	Sum of Squares	df	Mean Square	RMSE
Regression	6053.17	6	1008.86	
Error	221.55	1	221.55	14.88
Total	6274.72			

note: p-value is for two-sided t-te

R-square	F	Prob > F
96.47%	4.55	.3441

UNCODED VALUES

Regression Results for % clean

	Coefficients	Std. Dev.	t-statistic	Prob>|t|
Intercept	5.80000	16.85982	0.344	0.7482
conc	0.77400	2.38434	0.325	0.7617
flow	1.60000	3.91983	0.408	0.7040
conc*flow	0.78100	0.55435	1.409	0.2317

A N O V A

Source	Sum of Squares	df	Mean Square	RMSE
Regression	4738.21	3	1579.40	
Error	1536.51	4	384.13	19.60
Total	6274.72			

note: p-value is for two-sided t-te

R-square	F	Prob > F
75.51%	4.11	.1028

3 Factor Factorial Design for 0-15wt% Ethoxy

NAME	conc	temp	flow
HIGH	15	70	6
LOW	0	25	1

Run	conc	temp	flow	% clean	Predicted
1	0	70	6	16.5	18.275
2	0	25	1	6.2	7.975
3	0	70	1	8.6	6.825
4	15	25	6	66	67.775
5	15	70	6	88	86.225
6	0	25	6	14.3	12.525
7	15	25	1	29	27.225
8	15	70	1	37	38.775

coded inputs for regression

conc	temp	flow	conc*temp	conc*flow	temp*flow
-1	1	1	-1	-1	1
-1	-1	-1	1	1	1
-1	1	-1	-1	1	-1
1	-1	1	-1	1	-1
1	1	1	1	1	1
-1	-1	1	1	-1	-1
1	-1	-1	-1	-1	1
1	1	-1	1	-1	-1

Regression Results for % clean

	Coefficients	Std. Dev.	t-statistic	Prob>|t|
Intercept	33.20000	1.77500	18.704	0.0340
conc	21.80000	1.77500	12.282	0.0517
temp	4.32500	1.77500	2.437	0.2479
flow	13.00000	1.77500	7.324	0.0864
conc*temp	3.17500	1.77500	1.789	0.3245
conc*flow	9.00000	1.77500	5.070	0.1240
temp*flow	1.72500	1.77500	0.972	0.5091

A N O V A

Source	Sum of Squares	df	Mean Square	RMSE
Regression	6056.02	6	1009.34	
Error	25.21	1	25.21	5.02
Total	6081.22			

note: p-value is for two-sided t-	R-square	F	Prob > F
	99.59%	40.05	.1204

UNCODED VALUES:

Regression Results for % clean

	Coefficients	Std. Dev.	t-statistic	Prob>|t|
Intercept	5.80000	7.18822	0.807	0.4650
conc	1.22667	0.67771	1.810	0.1445
flow	1.60000	1.67123	0.957	0.3926
conc*flow	0.48000	0.15756	3.046	0.0382

A N O V A

Source	Sum of Squares	df	Mean Square	RMSE
Regression	5801.92	3	1933.97	
Error	279.30	4	69.83	8.36
Total	6081.22			

note: p-value is for two-sid	R-square	F	Prob > F
	95.41%	27.70	.0039

NOMENCLATURE

		SI Dimensions
A	exponential constant	-
A_d	deposit area	m^2
D	diffusivity	m^2s^{-1}
D_0	initial diameter of bubble	m
c	concentration	moles dm^{-3}
C_{OH}	concentration of hydroxide ions	moles dm^{-3}
d	diameter	m
E_{act}	Activation energy	$J\ mol^{-1}$
k	removal constant	s^{-1}
k_0	swelling removal constant	s^{-1}
m	mass deposit	kg
n	reaction order	-
p	pressure pulse	$N\ m^{-2}$
R	molar gas constant	$J\ K^{-1}\ mol^{-1}$
R_a	arithmetic mean roughness	m
R_f	fouling resistance	$m^2K\ W^{-1}$
R_m	degree of cleaning	-
Re	Reynolds number	-
T	temperature	K
T_g	glass transition temperature	K
T_m	melting temperature	K
t	time	s
u	velocity	$m\ s^{-1}$
U	heat transfer coefficient	$W\ m^{-2}K^{-1}$

Greek symbols

θ	contact angle	Degrees
ρ	density	$kg\ m^{-3}$
τ	shear stress	$N\ m^{-2}$
μ	viscosity of solution	$N\ s\ m^{-2}$
δ	deposit thickness	m
λ	thermal conductivity	$W\ m^{-1}\ K^{-1}$

Subscripts

0	initial value
cmc	critical micelle concentration
d	deposit
f	friction
g	gas
i	interface
l	liquid
s	substrate
w	water

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