A NONINVASIVE STUDY OF MILK CLEANING PROCESSES: CALCIUM PHOSPHATE REMOVAL

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ABSTRACT

High temperature, high pH milk processing results in the formation of mineral rich deposits that are > 70% mineral and < 30% protein by weight. This research investigates the removal of P^{32} *labeled mixtures of calcium phosphate dihydrate (brushite,* $CaHPO_4 \cdot 2H_2O$*) and hydroxyapatite (*$Ca_5(PO_4)_3OH$*) from stainless steel tubes using a solid scintillation technique. Experiments were performed at pH values ranging from 2.86-7.82 and flow rates from 3.8-11.4 L/min. Previous cleaning models are reviewed and a mass transfer model is proposed which, when compared to the experimental results suggests that film removal is due to both dissolution and mechanical effects due to shear stress. A modified first order model is presented which incorporates the effects of the solvent flow rate and pH on decontamination rates. This first order model is in agreement with the experimental results over the range of pH and flow rates investigated.*

INTRODUCTION

Cleaning Processes

The fouling and cleaning of stainless steel surfaces is a large problem in food processing. These fouled surfaces lead to increased costs due to energy losses, maintenance, additional heat transfer surface area and process downtime (Perka *et al.* 1993). Sandu and Singh (1991) report that the cost of cleaning agents to remove milk deposits in pasteurization plants in the fluid milk industry is over 20 million dollars per year. In a recent study on the cleaning of heat exchangers and evaporators fouled with milk and whey, Jeurnink and Brinkman

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(1994) speculated that an optimal cleaning procedure could result in an annual savings of over 5 million Dutch guilders. These savings would result from a reduction in energy costs, cleaning agents and product losses. Pritichard *et al.* (1988) state that in the dairy industry, up to 42% of the available production time may consist of cleaning and sterilization processes. These potential economic and performance improvements are the driving force for the development of methods to both reduce and/or eliminate fouling and clean fouled surfaces more efficiently.

There are two general classes of contaminant residues; solids and liquids. These contaminants can be further classified as homogeneous or heterogeneous mixtures. In the food industry, surface cleaning is particularly challenging due to the heterogeneity of the fouling residues. This heterogeneity makes it difficult to design a standard protocol consisting of a single solvent or surfactant system to completely clean all surfaces. In the food industry, most cleaning and sanitation procedures consist of a series of steps (Plett 1985) which may include: pre-rinse, cleaning, inter-rinse, sanitizing, and post-rinse processes.

Cleaning in place (CIP) procedures minimize the requirements of time, labor, cleaning solvent, and energy associated with the dismantling of processing equipment (Wennerberg 1981). During CIP procedures while cleaning efficiency is maintained, it is difficult to verify the degree of internal surface cleanliness and the rate at which contaminants are removed from the surface. This limitation causes the chemical and food industries to use cleaning reagents and solvents inefficiently.

A quantitative description of cleaning techniques useful for food and chemical processing requires an understanding of the fundamental steps that govern the process. On a macroscopic scale, the following factors influence the degree of decontamination or cleaning achieved: (1) the physical and chemical properties of the substrate (e.g., morphology, hydrophobicity), (2) the chemical composition, microscopic crystal structure of the contaminant and its film thickness, (3) the temperature, composition and concentration of the decontamination reagents, (4) the contact time between solutions and contaminants, (5) the solubility of the residue in the solvents (6) the fluid microstructure and the degree of turbulence promoted during the decontamination operation and (7) interfacial phenomena. This research investigates how some of the aforementioned factors affect the removal of solid residues from metal surfaces.

In a typical cleaning experiment, an evaluation is made of the amount of contaminant either remaining on the surface or removed from the solid substrate. Approaches to the determination of contaminant remaining after cleaning include: the direct measurement of the amount left on the surface (e.g., gravimetric), an assessment of a physical property of the surface related to the amount of contaminant remaining (e.g., color, wettability, reflectance) or an evaluation of a characteristic contaminant component (e.g., chemical analysis, the presence of spores) (Jennings 1963; Kulkarni *et al.* 1975; Corrieu 1981; Plett 1985; LeClercq-Perlat and Lalande 1994). The aforementioned techniques, however, are limited to periodic inspection of closed vessels or disassembled equipment.

A number of early research methods have been discontinuous or invasive in nature. Continuous evaluation of the cleaning process may be done by monitoring the contaminant in the effluent (e.g., chemical analysis, fluorescence, conductivity). The pressure drop in the system may also provide an indication of the amount of residue present. The major drawback of these monitoring techniques is that in spite of an indication that no further soil is being removed, there is no guarantee that complete cleanliness has been achieved (Plett 1985). The main obstacle in the study of cleaning processes is the accurate assessment of the transport phenomena at the substrate-residue interface. Given the level of complexity associated with heterogeneous residues, it is not surprising that cleaning processes have so far eluded detailed quantification and modeling.

Milk Residue Formation and Cleaning

Milk fouling can be described as a heterogeneous reaction that causes the aggregation of β-lactoglobulin, α-lactoglobulin, caseins, and fat globules to a solid surface. Calcium phosphate contributes to growth of the deposit by creating "carboxylate" bonds between protein aggregates and precipitated minerals. The most common mineral components are calcium phosphate dihydrate (brushite) ($CaHPO_4 \cdot 2H_2O$) and octocalcium phosphates ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$) with hydroxyapatite ($Ca_5(PO_4)_3OH$), the least soluble form of calcium phosphate in milk, on the surface (Sandu and Lund 1985). These mineral deposits readily form on heat transfer surfaces because raw milk exhibits a high degree of supersaturation with respect to calcium phosphates. For operating temperatures close to 100C, the milk fouling deposits are composed of 50 to 60% protein, 30 to 35% minerals, and 15 to 20% fat (LaLande and Rene 1988). During high temperature processing (130-140C) the resulting high density deposit is composed of up to 75% minerals.

The mechanism of milk deposition on metal surfaces has been represented by several fouling models. There is still a great deal of debate as to whether the initial layer formed on stainless steel consists of protein or minerals (Belmar-Beiny and Fryer 1993). A defect-growth model considers the fouling of milk proteins and mineral salts to occur in three steps: development of a compact sublayer, granule formation, and deposit growth (Sandu 1989). The compact sublayer formed at metal surfaces is composed of calcium phosphate and protein. Active sites on the surface of the sublayer (called protuberances) provide anchors for the granules of large protein aggregates, causing the growth of a porous, spongy deposit with low density and high moisture content. Fat globules and microorganisms are also entrapped in this matrix.

There are several cleaning processes commonly used for milk residues. For example, a two-stage process removes proteins and fats with an alkaline solvent (e.g., NaOH) and mineral deposits by an acidic solution (e.g., HNO_3 or H_3PO_4). In contrast, during single-stage cleaning the residues are removed by use of formulated detergents, which may contain surface active agents, chelating agents, or sequestering compounds (Timperley and Smeulders 1987; Jeurnink and Brinkman 1994). Several cleaning studies have focused on the removal of heterogeneous mixtures of fats and proteins as a function of alkali concentration (Grabhoff 1989; de Goederon and Pritchard 1989).

The removal of milk proteins from stainless steel surfaces has been studied extensively; below 100C, the protein represents the majority of the milk fouling deposit and is easy to detect. At high temperatures, the milk fouling deposit consists primarily of minerals. The presence of a mineral residue after cleaning can provide nucleation sites for subsequent fouling (Fryer 1989). Bird and Fryer (1991) state that in cleaning milk fouling residues the removal of mineral films is an area that needs further investigation. The first phase of our research focuses on the removal of calcium phosphate residues representative of those formed during high temperature processing of dairy based products. The rate of contaminant removal was studied in the region of fully developed turbulent flow; the region of industrial cleaning processes.

The effects of pH, surface finish, and flow rates on the cleaning rates are examined in an effort to develop a mechanistic model to describe the cleaning process. We have developed a noninvasive technique wherein the radioactivity of fouling deposits on the internal surface of a cylindrical flow cell is monitored continuously using solid scintillation. The experimental system consists of a flow cell coated with calcium phosphate. As the cleaning solvent flows through the cell a solid scintillation detector measures beta emissions from P^{32} radio-labeled calcium phosphate films. Dissolution and shear models are developed to describe the removal of calcium phosphate from a cylindrical hard surface into a flowing solvent. This research will provide information to the food process industry for the development of improved methods of estimating milk deposit removal, and a better understanding of the mechanisms that govern the removal of contaminants from hard surfaces.

BACKGROUND AND PREVIOUS WORK

In 1961, Bourne and Jennings reported that the majority of cleaning studies had been performed in the textile/fiber industry (Bourne and Jennings 1961). They were among the first in the food processing industry to investigate the removal of food related residues from solid surfaces. Since that time, several studies have been published on the cleaning of pipes, again emanating from the food processing industry. Timperley (1981) showed that the cleaning achieved in a pipe could be related to the shear stress at the laminar boundary layer under turbulent flow conditions. He reported that the shear stress, and therefore the cleaning efficiency, in pipes of different diameters scales with linear velocity rather than Reynolds number. In another study, the soil removal rate and turbulent shear stress in pipes were simultaneously measured using a constant-temperature anemometer (Paulsson and Tragardh 1985).

In addition to the residue removal studies described above, several works have focused on the mechanisms by which residues are bound to solid surfaces. Bourne and Jennings (1961) studied and examined the relative influence of electrostatic and van der Waals forces on the adsorption behavior of proteins. They presented evidence that two kinds of bonding exist in soil systems. The first is a soil-soil cohesion bond, which is relatively weak compared to the second, soil-surface adhesion bond. In a related study, Nassauer and Kessler (1985) concluded that globular proteins with hydrophilic groups were bound to a surface primarily by electrostatic forces, whereas denatured whey proteins were primarily bound by van der Waals forces between the surface and hydrophobic groups.

There are several general and very pertinent reviews of cleaning in the food industry. Plett (1985) reviewed the cleaning of fouled surfaces in food processing equipment, focusing on equipment design, operating parameters, and surfactant solution characteristics. Another review, by Kulkarni *et al.* (1975), provides a comprehensive summary of cleaning in the food (especially dairy) industry. Corrieu (1981) discusses methods of evaluating cleanliness, cleaning mechanisms and kinetics, and the role of parameters such as: detergent nature and concentration, temperature, mechanical action, surface finish, type of soil. His conclusion was that a systematic, fundamental approach to understanding cleaning is still needed.

The main limitation to a number of the aforementioned studies is that the experiments are either discontinuous or invasive in nature. Gallot-LaVallee *et al.* (1982), used an optical detector to continuously and noninvasively measure the turbidity of the solvent after passing over a surface contaminated with milk. These authors, however, noted possible problems with the turbidity measurements taken downstream from the surface being cleaned. Noninvasive discontinuous techniques to evaluate the contaminant remaining on the surface include: gravimetric analysis, FTIR and the use of radioactive tracers. For example, Ottesen (1986) used infrared reflection spectroscopy to evaluate stainless steel tubing contaminated with thin films of hydrocarbon lubricants and metal oxides.

Several researchers have looked at the relative contributions of solubility (Linton and Sherwood 1950; Harriott and Hamilton 1965), dissolution (Murray 1987a,b) and shear-stress or mechanical effects (Beaudoin *et al.* 1995a,b; Jackson 1984; Timperley 1981) to the removal of contaminants from solid surfaces. Jackson (1984) found that significant cleaning required a minimum velocity; below the minimum velocity the fluid does not provide enough shear to remove a significant portion of the contaminant.

The Use of Radiotracers in Cleaning Studies

The use of radioactive tracers to study the cleaning of metal surfaces was first reported by Harris *et al.* (1950) as an alternative to the fluorescent dye, copper plate, and water spreading analytical tests. The sensitivity of the radioactive tracer technique was reported to be up to 100 times better than other methods in use at that time. In early studies, Jennings (1961) reported an extremely high correlation between the gravimetrically determined percent soil removed and the percent radioactivity removed from stainless steel. In one of the first models describing the removal of food products from solid surfaces, Jennings *et al.* (1957) studied the effects of time, temperature, and solvent type (e.g., pH) on the removal of P^{32}-labeled dried milk from solid surfaces. Peters and Calbert (1960) also reported that when P^{32} was incorporated into bacterial cells that were suspended in the test milk soil, there was a linear response between the weight of soil removed and the radioactive count removal.

Radiotracers have also been utilized to study the rate of deposition and removal of contaminants as a function of the nature of the surface (e.g., morphology) (Pflug *et al.* 1961; Peters and Calbert 1960; Perka *et al.* 1996). Masurovsky and Jordan (1960) investigated the removal of P^{32} labeled bacteria from stainless steel, aluminum, glass and Teflon during ultrasonic cleaning. They reported that the type of surface roughness influenced the degree of bacterial retention and the subsequent growth of the organisms.

More recently, radioactive species have been used to study the decontamination of nuclear facilities prior to decommissioning. In these studies, the contaminant species (e.g., metal oxides) is already radioactive. The main goal of these studies has been to investigate the chemical reactivity of the decontamination reagents with the contaminant films (Bradbury *et al.* 1983; Murray 1986). In contrast to earlier radioactive tracer studies, a solid scintillation technique will enable us to continuously evaluate the interface between the substrate and the contaminant during the decontamination process. This approach will eliminate disturbance of the contaminant-solvent interface when the substrate is removed from the cleaning solution prior to evaluation.

MATERIALS AND METHODS

A heterogeneous mixture of P^{32} labeled calcium phosphate in slurry form is used to coat a stainless steel experimental tube cell. The P^{32} labeled residues emit energy in the form of beta particles. The amount of P^{32} species present on the pipe surface can be detected using solid scintillation. The fraction of β-particles transmitted through the stainless steel is defined as

$$N(t')/N(0)=\exp(-\mu_m t') \tag{1}$$

where N(0) is the number of incident beta particles, N(t') is the number of beta particles transmitted through a thickness t', and μ_m is the mass absorption coefficient (Tsoulfanidis 1983).

The following sections describe the experimental cleaning apparatus, the method used to prepare the calcium phosphate coatings, the chemical properties of the slurries and the physical nature of the resulting residues. Presentation of the results of the decontamination experiments are followed by a discussion of the application of theoretical kinetic and mass transfer models to the experimental data.

Experimental Apparatus

The aqueous cleaning solvent was placed in a solvent feed tank and pumped through the 304 stainless steel piping by a Micropump Model 101-415 pump (see Fig. 1). The flow rate was monitored by an Omega flow meter. The spent solvent is collected in an effluent storage tank. The 304 stainless steel tube cell (see Fig. 2) consisted of a thin inner sheath (thickness = 0.1016 mm) and an outer protective tube (OD = 12.7 mm, length 60 mm) with a window opening for connection to the scintillator detector. The inner diameter of the system piping was the same as the ID of the tube cell. The test cell is placed far enough downstream of the inlet to insure fully developed turbulent flow. Two types of surface finishes were used in the tube cell; a #4 finish, which is a finely polished surface, and a #63 finish, which is visibly rough. The precision engineered stainless steel tube cell was designed to allow a high transmission rate of beta particles through the cell window. The rate at which beta particles leave the tube cell window is measured by a CaF_2 solid-scintillation detector (Fig. 2). Using the approximation from Eq. 1, 48% of the β-particles emitted from the inner surface of the window were able to pass through the stainless steel.

The light signal from the CaF_2 scintillation detector (Bicron) is sent to a photo-multiplier tube, amplified and converted to an electronic signal. The amplified signal is transmitted through a Tennelec TC145 preamplifier, a Tennelec TC241 amplifier, and an Oxford multi-channel scalar that converts the raw signal to net counts. This signal is sent in digital form to an IBM 386 compatible personal computer which displays and stores the signals.

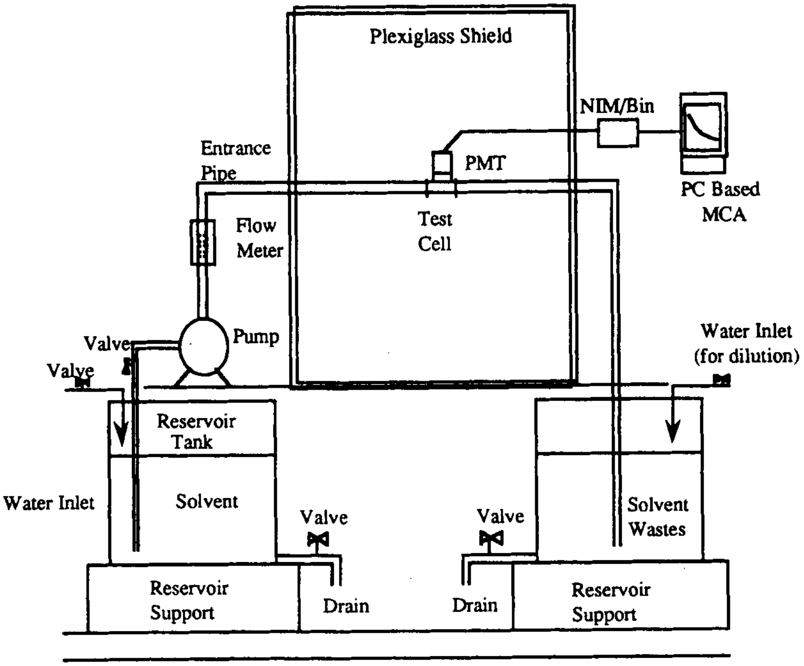

FIG. 1. SOLID SCINTILLATION EXPERIMENTAL FLOW SYSTEM

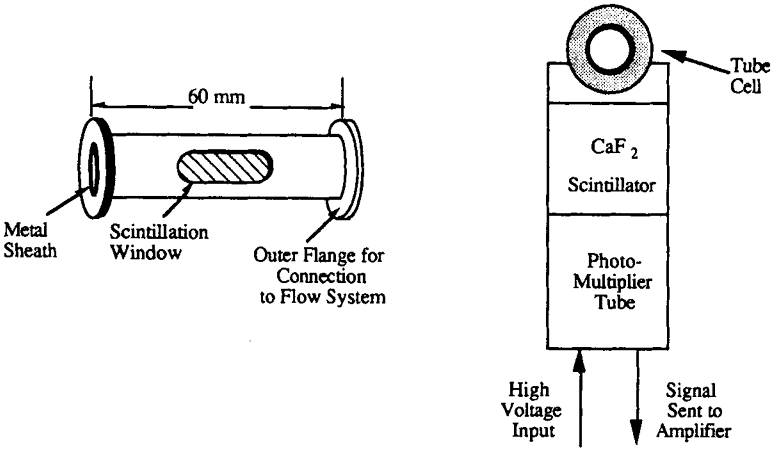

FIG. 2. EXPERIMENTAL TUBE CELL FOR SOLID SCINTILLATION EXPERIMENTS

Preparation of Calcium Phosphate Slurry and Cleaning Experiments

The calcium phosphate slurry is a mixture of the hydroxyapatite and the brushite compounds commonly found in milk fouling residues. The Ca/P ratios in this study were selected to represent calcium phosphate formulations found in high temperature fouling residues.

The coatings in the tube cell were formed by drying calcium phosphate slurries made from phosphoric acid and calcium hydroxide. One hundred μL of radio-labeled 2×10^{-7} M phosphoric acid (DuPont Chemical) and 100 μL of unlabeled 1 M phosphoric acid (Fisher Scientific) were mixed with 5.3 mL of a 1.057×10^{-2} M calcium hydroxide solution (Fisher Scientific). The phosphoric acid/calcium hydroxide mixture was allowed to equilibrate in a centrifuge tube for 24 h at 25C. The resulting solution was centrifuged (Fisher Scientific; Marathon 6K) for 50 min at 5000 rpm and the supernatant was drained. A 250-watt infrared lamp (Fisher Scientific; Infra-Rediator) was used to dry the calcium phosphate slurry at approximately 89C for 2 h. The slurry was reconstituted by adding 2 mL of distilled water to the centrifuge tube and stirring with a micro-stir bar for 15 min.

The coating in the test cell was created by injecting 1 mL of the reconstituted calcium phosphate slurry into a stainless steel tube cell capped at both ends. The slurry was dried by rotating the tube cell horizontally at 60 rpm under the 250 watt infrared heat lamp at 89C for 12 h. To test the uniformity of the film, a tube cell without a window was coated with radio-labeled calcium phosphate and allowed to dry. The counts emitted from the cell were measured at different angles using the solid scintillation technique. The rotational coating varied only 1.33% over the range of angles measured. The error associated with measuring the coatings is approximately 1.0%.

The average mass of calcium phosphate mixtures used to coat the tube cell was 3.14 ± 0.198 mg. The thickness, t_{film}, on the surface of the tube cell was estimated from the dimensions of the cell and the density of the calcium phosphate (2.306 g/cm^3):

$$M=\rho_0 \pi (R^2-r_0^2) L \tag{2}$$

$$t_{film}=R-r_0=0.692 \mu m \tag{3}$$

where M is the total dry mass of the film deposited in the tube cell, ρ_0 is the density of calcium phosphate, R is the radius of the tube cell, and r_0 is the initial distance from the center of the tube cell to the solid surface of the film. This value for r_0 was used for model calculations.

The tube cell was tightly secured in the flow apparatus so that the window was flush against the solid scintillation detector (Fig. 2). Before the flow was started, the activity of the coating was measured for one minute. When the pump was turned on, the activity was measured in 10 s intervals. In initial cleaning studies, fresh solvent (reverse osmosis water) was used; the length of the experimental run was limited by the size of the solvent reservoir (189 L) and the flow rate of the solvent (3.8-11.4 L/min). Changes in the pH values of the solutions were achieved by adding a solution of 12.1 normal hydrochloric acid, HCl (Fisher Scientific) to the water. Experiments were conducted at flow rates and pH values ranging from 3.8-11.4 L/min and 2.86 to 7.82, respectively. The majority of the experiments occurred on a #63 test cell. Duplicate runs were performed under all conditions except the flow rate of 3.8 L/min for the #4 cell at a pH of 3.24. All experiments were conducted at room temperature.

Solubility Determination

Studies were performed using P^{32} radio-labeled calcium phosphate to determine equilibrium solution concentrations. The solubility value can be used in the dissolution based model to define the concentration at the interface between the solid and the solution. Calcium phosphate slurries were prepared in an identical manner to that used in coating the experimental flow cell. All samples (i.e., for calibration and solubility studies) were equilibrated for three weeks at room temperature, followed by liquid scintillation measurements. The calibration solutions were prepared by completely dissolving a specific amount of calcium phosphate in a strongly acidic solution (pH=2.0). Different amounts of this calibration solution were then pipetted into a liquid scintillation cocktail (ICN; CytoScint™) and counted using a liquid scintillator (Packard 1500 Tri-Carb® Liquid Scintillation Analyzer).

Four solubility studies were performed over an eight month period over the range of solution pH values used in the cleaning studies. There was limited reproducibility in the four studies conducted (see Fig. 3). The solubility experiments reported here are presented as a function of the pH of the solvent before it was added to the calcium phosphate mixture. The experimental solubility was compared with literature solubility values for brushite (Driesseus and Verbeek 1990). The literature solubility values are at the pH of the solvent after equilibrium was reached. The differences in the solubility values of pure brushite in the literature are most likely a result of the calcium phosphate being a mixture of brushite and hydroxyapatite and the difference in the reporting of the solvent pH values. The solubilities were measured at the following pH values: Study A-> 2.65-3.88; Study B-> 2.0-4.0; Study C-> 2.72-3.36; Study D-> 2.72-3.36; Study E-> 2.81-3.24.

Determination of Calcium Phosphate Formulation

The Ca/P ratio in heterogeneous milk deposits has been reported to be approximately 1.5 (Lyster 1965; Jeurnink and Brinkman 1994). Brushite has a

Ca/P ratio of 1.0 and the Ca/P ratio of hydroxyapatite is 1.67. It has been reported in the literature that calcium phosphates created under acidic conditions generally form brushite $(CaHPO_4)\cdot 2\ H_2O$ and hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (Driesseus 1990). Hence, a solution with an initial $Ca(OH)_2/H_3PO_4$ ratio equal to 0.5 leads to a brushite-rich precipitate. A solution with an initial $Ca(OH)_2/H_3PO_4$ ratio of 2.0 results in a hydroxyapatite-rich precipitate.

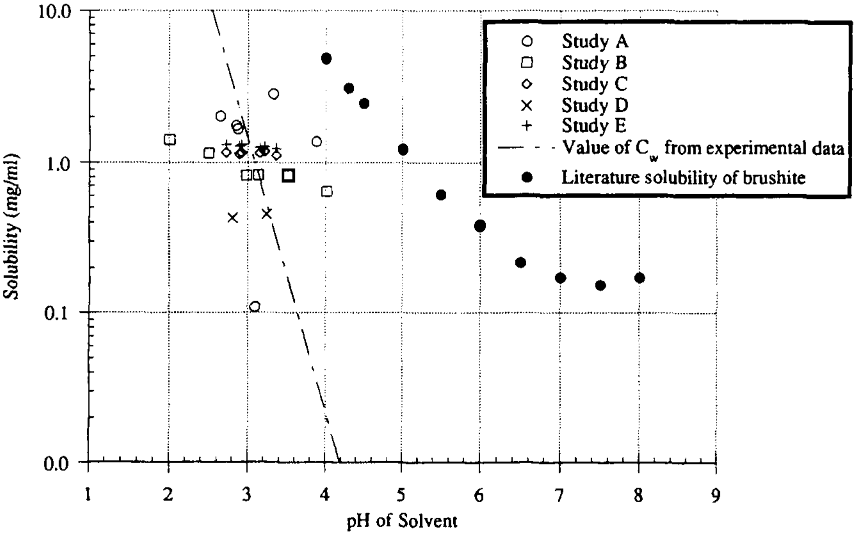

FIG. 3. CHANGES IN CALCIUM PHOSPHATE SOLUBILITY WITH pH (COMPARED WITH LITERATURE SOLUBILITY FOR BRUSHITE) (DRIESSEUS AND VERBEEK 1990)
Calcium phosphate solubility determined using liquid scintillation techniques.
Literature solubility of brushite presented at equilibrium pH values.

To determine the type of calcium phosphate mixture used in the decontamination experiments, the Ca/P ratios of unlabeled slurries were measured. The precipitates were analyzed for calcium and phosphorus contents using atomic absorption (AA) and UV-visible spectrometry, respectively. Initial solution molar ratios of $Ca(OH)_2/H_3PO_4$ of 0.5, 1.0, and 2.0, resulted in Ca/P ratios of the precipitates of 1.00, 1.12, and 1.51, respectively. The Ca/P ratio in all slurries used in the decontamination experiments was approximately 1.1.

The solution in equilibrium with the precipitated calcium phosphate was also analyzed to ascertain the calcium phosphate formulation. Inductively coupled plasma atomic emission (ICPAE) spectrometry analysis (Perkin Elmer; Plasma 2000) was performed on dilutions of supernatant in equilibrium with calcium phosphates with DI water. In this test, calcium phosphate was made by mixing

100 μL of unlabeled 1 M phosphoric acid with 5.3 mL of 1.057 × 10^{-2} M calcium hydroxide solution. One hundred microliters of DI water were added to compensate for the 100 μL of labeled phosphoric acid. This combination of calcium hydroxide and phosphoric acid yields an initial $Ca(OH)_2/H_3PO_4$ ratio of 0.56. The supernatant had a phosphorus concentration of 7.17 × 10^{-3} M and a calcium concentration of 7.62 × 10^{-3} M. The measured pH of the supernatant solution was 5.45. A study by Patel *et al.* (1974) found the calcium concentration of brushite in equilibrium with a solution having a pH of 5.41 to be 3.74 × 10^{-3} M; their value is slightly lower than those found in this study.

RESULTS AND DISCUSSION

Cleaning Experiments

The effect of the following parameters on the removal rate of calcium phosphate were studied: solvent type, flow rate, solvent pH, drying temperature of tube cell and surface finish. In the cleaning experiments, the net counts detected by the solid scintillator were assumed to correspond to the amount of calcium phosphate film on the cell window. Water is a low density material and absorbs the energy of beta particles; hence there will be a reduction in the signal when water is present in the cell. An experiment was performed to measure the signal dampening associated with a solvent blocking beta particle emissions. A flow cell was coated with 6.28 mg of P^{32} labeled calcium phosphate. The flow cell was then mounted vertically against the solid scintillator, and the signal was measured from the dry cell and after the cell was slowly filled with 4 mL of DI water. Approximately 60% of the signal was blocked by the DI water. This is on top of the 48% detectable signal mentioned earlier due to the density of the stainless steel.

Because of the water dampening effects, the data collected during decontamination experiments have been normalized to the signal strength after 30 s of solvent flow. Hence, the beginning of the run (i.e., time equal to zero on the plots) is actually 30 s into the collection of experimental data. This normalized (or time modified) signal indicates the amount of P^{32} remaining, which is proportional to the fraction of calcium phosphate remaining on the stainless steel. The half-life of P^{32} is 14 days; hence, the decontamination data are presented as fraction remaining versus time to eliminate the variation in the initial counts between experiments.

Reverse osmosis water was used in the cleaning experiments; the large differences in the tap water quality caused variations in the cleaning results. The reproducibility of the decontamination experiments is presented for runs using RO water as the solvent. Figure 4 shows the results of decontamination experiments performed at flow rates of 3.8 L/min and 11.4 L/min. This data indicates that the use of the rotational coating technique and RO water as a solvent produced consistent, reproducible cleaning results.

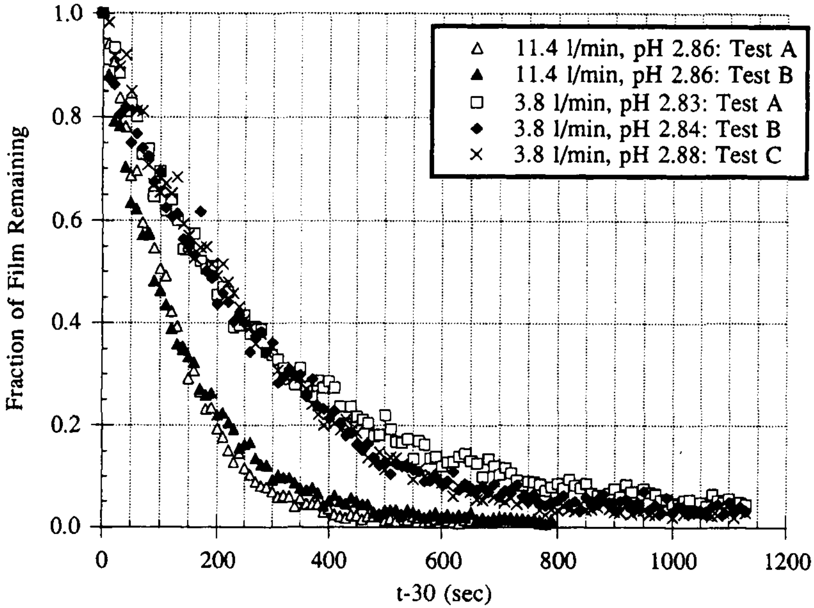

FIG. 4. REPRODUCIBILITY OF RO WATER EXPERIMENTS PREPARED USING A ROTATIONAL COATING, SOLVENT FLOW RATES OF 3.8 L/MIN AND 11.4 L/MIN (#4 TUBE CELL)

Initial decontamination rates were determined by performing a linear regression over the first 100 s of a particular decontamination experiment. The effect of pH and flow rate on decontamination rates is illustrated in Fig. 5; as the solvent flow rate is increased from 3.8 L/min to 11.4 L/min there is a 65% increase, in the initial cleaning rate. The increase in removal of calcium phosphate with decreasing pH can be attributed to the dependence of calcium phosphate solubility on pH. At the highest pH value (7.82) there is no significant removal in the first 100 s. It should be noted that the scatter at the high pH is due to the scatter in the raw data at low count rates. The benefits of a low pH on cleaning rates is also observed at lower flow rates. This is consistent with observations made by Jeurnink and Brinkman (1994) and others on the use of an acidic solution to remove mineral films produced in milk fouling.

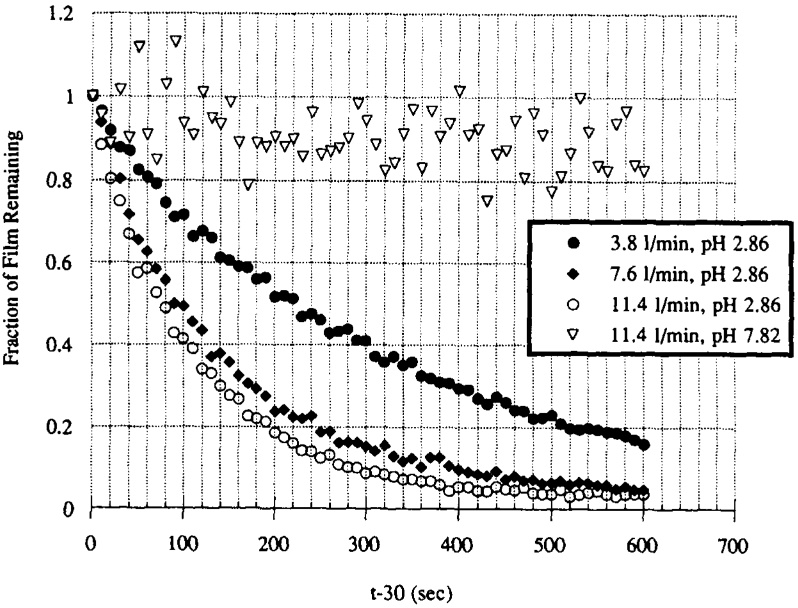

FIG. 5. EFFECT OF FLOW RATE AND pH ON DECONTAMINATION
Note: scatter in high pH data due to low activity and corresponding low count rate of sample.

A limited number of tests were done to evaluate the role of surface finish (#63 and #4 finishes) on the rate and extent of surface cleaning. Under the experimental conditions of our tests in the removal of solid calcium phosphate residues, Fig. 6 suggests that the surface finish had little effect on both the initial and final decontamination rates.

Scanning Electron Microscopy (SEM) Studies

The morphology of the calcium phosphate films was determined indirectly from scanning electron micrographs (SEMs). In this study, 1 cm square stainless steel coupons made of the same 304 stainless steel as the experimental tube cells were coated with calcium phosphate slurries and dried under the infrared heat lamp to evaporate the water, producing a solid residue. After drying, the coated samples were suspended in solutions of varying pH; the pH was adjusted by mixing HCl acid in distilled water at 25C. To simulate the cleaning process a constant flow of solvent was provided by a magnetic stirbar. After cleaning, the test coupons were removed and allowed to dry overnight at room temperature. Scanning electron micrographs of the dried samples are shown in Fig. 7.

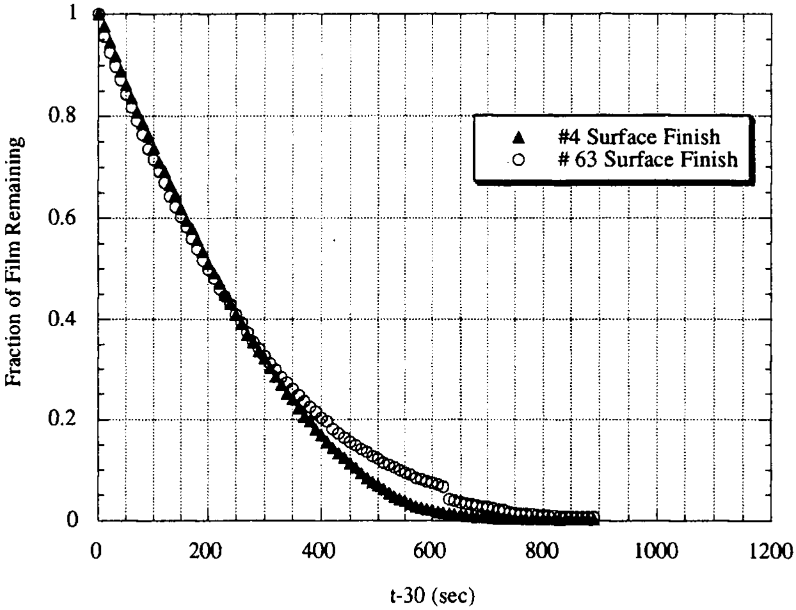

FIG. 6. EFFECT OF SURFACE FINISH ON RO WATER EXPERIMENTS PERFORMED AT A SOLVENT FLOW RATE OF 7.6 L/MIN AND AN AVERAGE SOLVENT pH OF 2.86

The pH values of the solutions were selected based on the pH values of solvents used in decontamination experiments. After 30 s of cleaning at a pH of 2.89, Fig. 7a indicates that there are several particles of calcium phosphate present and the stainless steel is visible. Figure 7b represents twenty minutes of cleaning in a solution with a pH of 2.89. Under these conditions, the majority of the calcium phosphate has been removed from the stainless steel surface.

The removal of the residue is due to the dissolution of the calcium phosphate on the surface and the breaking of the bonds between the residue and the stainless steel. The projected surface area of the crystals was found to range from 2.5×10^4 to $1.0 \times 10^5 \mu m^2$ with an average area of 6.5×10^4 μm^2. The morphology of the calcium phosphate residue is similar to that reported by Timperley and Smeulders (1987) for mineral residues.

MECHANISMS OF DEPOSIT REMOVAL AND DECONTAMINATION MODELS

The theoretical models used to describe cleaning in the chemical, nuclear and food industries range from purely empirical relationships to models based

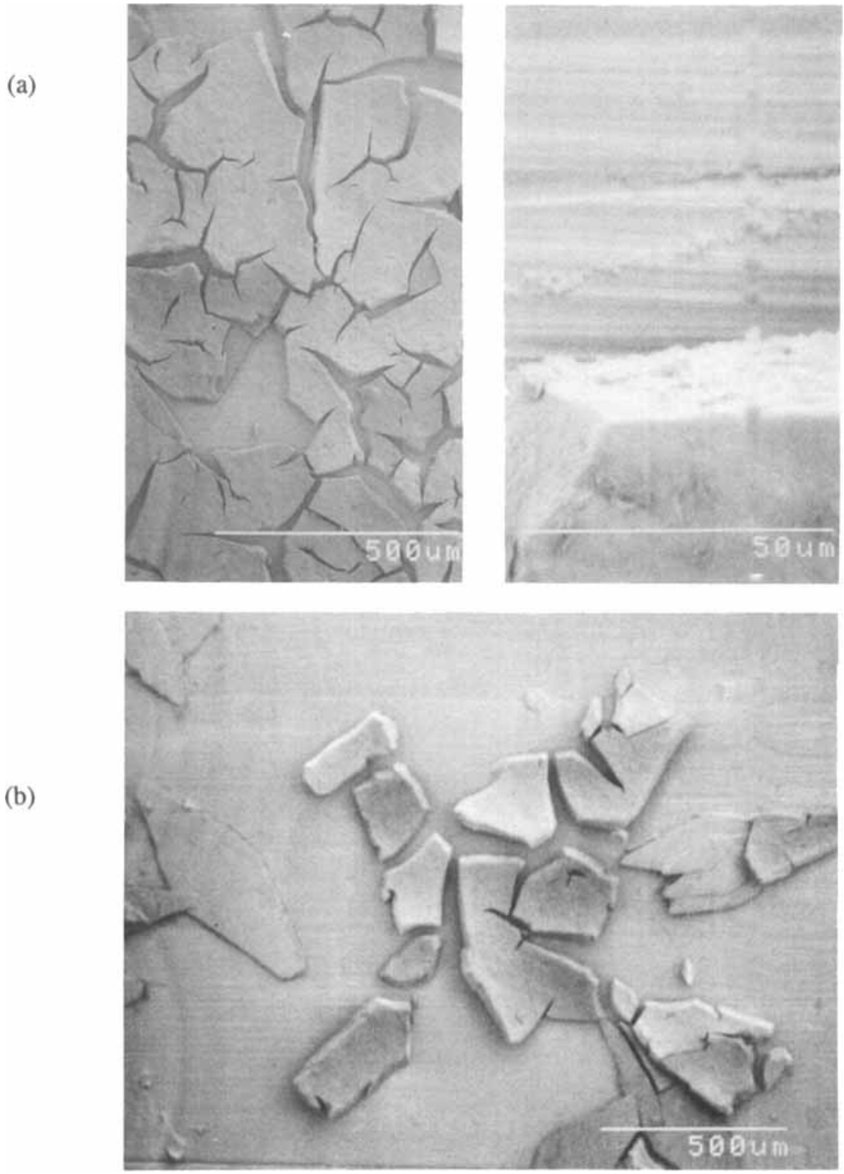

FIG. 7. SCANNING ELECTRON MICROGRAPHS: (a) CALCIUM PHOSPHATE COATING AFTER 30 S OF CLEANING AT A pH OF 2.89 (30/300 X) MAGNIFICATION, (b) CALCIUM PHOSPHATE COATING AFTER 20 MIN OF CLEANING AT A pH OF 2.89 (30X MAGNIFICATION)

on mass transfer principles. There are three basic approaches used to model contaminant removal: (1) an empirical model which attempts to fit the data based on solvent or solute concentrations (2) a dissolution based mass transfer model that accounts for the contaminant solubility, and the transport of material away from the surface and (3) models which evaluate the removal of large aggregates of contaminant as a function of shear stress. Table 1 contains a brief summary of some models along with the contaminants to which the models have been applied. Jennings (1957) was one of the first to develop models to describe the removal of food products from solid surfaces. Jennings used a first order (in contaminant concentration) empirical model for the rate of removal of milk residues as a function of the concentration of hydroxyl ions ($C_{OH,B}$) and the concentration of the contaminant to be removed (C_x):

TABLE 1.
EXAMPLES OF DECONTAMINATION MODELS USED IN FOOD, CHEMICAL AND NUCLEAR INDUSTRIES

Contaminant Type	Reaction Order	Model	Author(s)
Dried Milk	*1st Order* Limited by Reaction	$\frac{dC_x}{dt} = -k C_x C_{OH,B}$	Jennings (1957)
Dirt and Scale Formed in Condensers	Dependent upon kinetic energy of fluid and deposit thickness	$\frac{dM}{dt} = -k \tau x_{\text{[illegible]}}$	Kern and Seaton (1959)
Milk Residues	*Two stage cleaning model* 1st stage: zero order 2nd stage: removal of intermediates	$\frac{dM}{dt} = b_5[1 - \exp(b_6 t)]$ for $t < M_0 / b_5$ $\frac{dM}{dt} = b_5[\exp(b_6(M_0 / b_5)) - 1]\exp(-b_5 t)$ for $t > M_0 / b_5$	Gallot-LaVallee *et al.* (1982)
Metal Oxides	*Zero Order* Limited by dissolution *1st Order* Limited by dissolution	Dense film no pores $\frac{dM}{dt} = -k_1$ Porous film $\frac{dM}{dt} = -kM$	Murray (1987)

$$\frac{dC_x}{dt} = -kC_x C_{OH,B} \tag{4}$$

where k is an empirical rate constant. When compared to experimental data, Jennings found that the model is only valid up to the removal of 60% of the initial contaminant. In their study, the lack of continuous measurements of the mass of contaminant made it difficult to make an accurate assessment of cleaning kinetics.

The cleaning process is often represented as occurring in four distinct stages (Harper 1972): (1) transport of the solvent to the surface of the contaminant to be removed, (2) wetting and penetration of the contaminant by the solvent, (3) transport of the contaminant away from the solid-liquid interface, and (4) prevention of contaminant redeposition onto the clean, solid surface. Although, each of the aforementioned stages can be described using transport phenomena, researchers find it difficult to accurately model each stage using fundamental transport phenomena.

Schlussler (1970) attempted to simplify the mechanisms of Harper with the objective of developing a transport based model to describe cleaning behavior:

$$\frac{dN}{dt} = -\frac{D_{soil}A}{z_w}(C_w - C_b) \tag{5}$$

where dN/dt is number of moles dissolved per unit time, C_w is the concentration of contaminant in equilibrium with solvent, C_b is the concentration of soil in bulk solution, A is the surface area of soil, D_{soil} is the diffusivity of the contaminant in the solvent, and z_w is the thickness of the equivalent boundary layer. Schlussler's model assumed the following: (1) the first and third stages were controlled by diffusional mechanisms across an equivalent hydrodynamic boundary layer created by the fluid stream, (2) the dissolved contaminant diffuses more slowly than the solvent itself and (3) stage three, the transport of contaminant away from the solid-liquid interface was the rate-limiting step for the overall removal of contaminant.

Gallot-LaVallee *et al.* (1982), were among the first to develop a continuous, noninvasive technique for measuring the removal of contaminant films. They applied their optical technique to measure the decontamination of fouled tubes and proposed a two-stage cleaning model (see Table 1). The first stage, a zero-order step, represents the formation of an intermediate component, similar to an active site complex in a heterogeneous catalytic reaction. The second stage represents the removal of intermediate components through the equivalent concentration boundary layer.

Kern and Seaton studied the fouling and cleaning of heat transfer equipment in the nuclear industry (Kern 1959; Murray 1987). Kern and Seaton's model is based on the assumptions that: (1) contaminant removal is due to the shearing action of fluid passing the surface; (2) the contaminant film is removed as chunks of material at random planes of weakness; and (3) these planes of weakness are likely to occur at any depth in the residue. The rate of deposit removal is described in terms of the thickness of the deposit, x_{thick} (see Table 1). In this relationship k is an arbitrary rate constant, τ is the shear stress at the interface, and M is the mass of the deposit. Rewriting the shear stress in terms of the velocity, the rate of deposit removal is:

$$\frac{dM}{dt} \propto v^{1.75}. \tag{6}$$

Studies performed by Jackson (1984) on the removal of tomato paste from heat exchanger plates found that significant cleaning required a minimum velocity; below the minimum velocity the fluid does not provide enough shear to remove a significant amount of the particular contaminant.

Models of Calcium Phosphate Decontamination

The data from the calcium phosphate decontamination studies in this work will be evaluated using two different approaches. The first approach starts with a model for the dissolution of a solid cylindrical surface into a flowing solvent. This approach is often used to describe the removal of individual molecules of a species into a fluid. The second technique is based on the kinetic modeling work of Jennings; the resulting modified first order model is an empirical fit of the data as a function of pH and velocity.

Dissolution Model of Contaminant Removal. A standard mass transfer model can be used to describe the dissolution of a solid from the inside of a cylindrical surface. The following assumptions are made in the development of the model: (1) a smooth contaminant surface, (2) fully developed flow, and (3) a concentration at the solid-liquid interface equal to the solubility of the contaminant in the solvent. The molar flux, J, of a contaminant species into a bulk solvent can be described as:

$$J = -k_m(C_b - C_w) \tag{7}$$

where C_b is the bulk concentration of the contaminant (e.g., calcium phosphate), C_w is the concentration of contaminant at the solid-liquid interface (assumed to be the solubility), and k_m is the mass transfer coefficient. A mass balance performed on a differential volume element of solid within the pipe results in the local rate of change of the mass within the differential control volume (see Fig. 8):

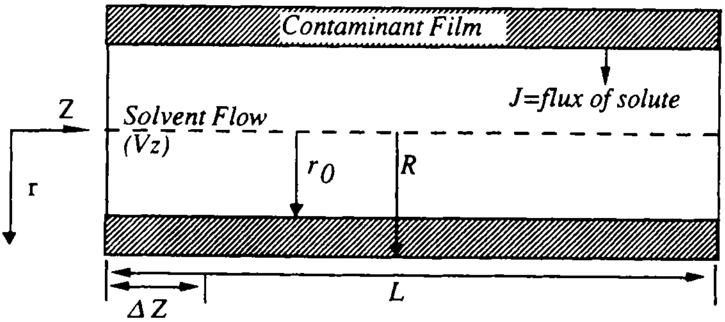

FIG. 8. CYLINDRICAL CONTROL VOLUME USED FOR DISSOLUTION MODEL

$$\frac{\partial M'(z)}{\partial t} = -J(z)A\bar{M} \tag{8}$$

where A is the surface area of the control volume, and $\bar{M}$ is the average molecular weight of the material in the film. Using the parameters indicated on the control volume in Fig. 8, Eq. (8) can be written as:

$$\frac{\partial}{\partial t}\left[\rho_0 \Delta z \pi (R^2 - R_i^2)\right] = -J(z)\bar{M}2\pi R_i \Delta z \tag{9}$$

where ρ_0 is the density of the calcium phosphate film, R is the radius of the cylinder, and R_i is the radius of the film at a given axial position and time. Incorporating the definition of the molar flux into Eq. (9) results in the following expression for the rate of change in the radius of the film:

$$\frac{\partial R_i}{\partial t} = \frac{-k_m(C_b - C_w)\bar{M}}{\rho_0} \tag{10}$$

The radius of the film at a dimensionless distance Z:

$$Z = \frac{z}{L} \tag{11}$$

from the inlet to the tube can be expressed as a dimensionless parameter:

$$\phi = \frac{R_i}{r_0} \tag{12}$$

where r_0 is the initial radius of the solid and L is the length of the tube cell. Equation 10 can be expressed as:

$$\frac{\partial\phi}{\partial\eta}=\frac{-k_m\bar{M}L}{\rho_o\langle v_z\rangle r_o}\theta(Z,\eta) \tag{13}$$

where Θ is the concentration gradient:

$$\theta=(C_b-C_w) \tag{14}$$

and the dimensionless time is expressed as:

$$\eta=\frac{t\langle v_z\rangle}{L} \tag{15}$$

The concentration, Θ, can be expressed as a differential equation from a mass balance on the contaminant in the liquid phase:

$$\frac{\partial\theta}{\partial\eta}+\frac{\partial\theta}{\partial Z}=-\frac{2k_m}{r_o}\frac{L}{\langle v_z\rangle}\theta \tag{16}$$

The boundary conditions and the initial condition for Eq. 16 are:

$$\begin{aligned}\theta&=-C_w && @Z=0\\ \theta&=-C_w && @\eta=0\end{aligned} \tag{17}$$

Equation 16 can be expressed in terms of dimensionless correlation's as:

$$\frac{\partial\theta}{\partial\eta}+\frac{\partial\theta}{\partial Z}=-2\left[\frac{Sh}{ReSc}\right]\frac{L}{r_o}\theta \tag{18}$$

where

$$Sh = 0.0172(Re)^{0.86}(Sc)^{0.33} \text{ and } Sc = \frac{\mu}{\rho D_{AB}} \tag{19}$$

Solving Eq. 18 using Laplace Transforms

$$\begin{aligned}\theta&=-C_w e^{-\beta Z} \text{ for } Z<\eta\\ \theta&=-C_w e^{-\beta\eta} \text{ for } Z>\eta\end{aligned} \tag{20}$$

where

$$\beta=2\left[\frac{Sh}{ReSc}\right]\frac{L}{r_0}. \tag{21}$$

At long times ($\eta > 1$) the average dimensionless radius of the solid phase over the length of the film is

$$\bar{\phi} = 1 + \frac{\bar{M}C_w}{2\rho_0}\left[1-e^{-\beta}\right]\eta \text{ for } Z<\eta \tag{22}$$

The total mass of the film can be expressed as:

$$M(\eta)=\rho_0\pi L r_0^2\left[\left(\frac{R}{r_0}\right)^2-\bar{\phi}^2\right] \tag{23}$$

(Grant *et al.* 1996). The normalized film residual is defined as the mass of film remaining divided by the mass of initial film and can be written as (Webb 1994):

$$\frac{M(\eta)}{M(0)}=\frac{\left[\left(\frac{R}{r_0}\right)^2-(1+\kappa\eta)^2\right]}{\left[\left(\frac{R}{r_0}\right)^2-1\right]} \tag{24}$$

where:

$$\kappa=\frac{\bar{M}C_w}{2\rho_0}[1-e^{-\beta}] \tag{25}$$

and β is defined as a function of key dimensionless transport variables. Incorporating the definitions for Re, Sc an expression for the effect of bulk velocity on the rate of removal can be defined as

$$\frac{\partial M(t)}{\partial t}=-\pi L r_0\bar{M}C_w\frac{[2^b a R^{b-1} v_z^b \rho^{b-1} Sc^{c-1}]}{\mu^{b-1}}. \tag{26}$$

The rate of removal of calcium phosphate is a function of the velocity of the bulk fluid raised to the *b* power. The dissolution model developed indicates that if dissolution is the sole mechanism of removal, the rate of removal should be approximately proportional to the velocity to the 0.86 power.

Development of a Modified First-Order Decontamination Model. The velocity dependence in the first model is used to describe molecular diffusion of CaP molecules from the surface to the bulk solution. The dissolution model does not account for the role of shear in removing large contaminant aggregates. The SEMs, however, indicate that during the cleaning process, the calcium phosphate is dislodged from the metal surface as large aggregates. Several researchers have reported that both mechanical and dissolution mechanisms are involved in the removal of contaminant films (Jennings 1965; Linton and Sherwood 1950; Harriott and Hamilton 1965). Even though it is clear that both mechanical and dissolution mechanisms are important, most cleaning studies focus on a single mechanism.

The rate of cleaning of various fouled surfaces has been reported by several authors to have a first order behavior (Jennings 1957; Kern 1959; Gallot-LaVallee 1982; Murray 1987a,b). The proposed rate equation usually has the following form:

$$\frac{dM}{dt} = -kM, \tag{27}$$

where k is a first-order rate constant. The initial mass on the surface is defined as:

$$M = M_0 \qquad @t=0. \tag{28}$$

Incorporating the initial conditions into the rate equation, results in the following expression for the fraction of the film remaining:

$$\frac{M(t)}{M_0} = \exp(-kt). \tag{29}$$

In the modified first order model, a numerical fit of the decontamination data has been made which incorporates the velocity and pH effects. The first order rate constant, k, is expanded to account for the pH of the solvent and the flow rate. Since the experimental data has been normalized to the mass of the film at 30 s (instead of the mass of film at t=0), the least square fit was performed using a function of the following form based on the exponential behavior of the data:

$$\frac{M(t)}{M(30s)} = \exp[\alpha v_z^n(t-30)], \tag{30}$$

where α and n are fitted parameters (based on the experimental data), v_z is the velocity of the fluid, and t is the time in seconds. The statistical analysis of the data was conducted using an EXCEL spreadsheet program. The same program was used for the curve-fitting presented later in this paper. The parameter α was determined separately for each unique solvent pH so that a dependence of α on hydronium concentration could eventually be determined. The parameters α and n were calculated by minimizing the sum of the squares of the relative error over the first 600 s of a cleaning experiment. The parameter n was determined by fitting both α and n to 27 experiments performed at pH values of 2.81, 2.86, and 2.93. A weighted average was found for n (0.70); this value was used to independently determine the values of α. After computing values for α, the parameter was fit to an equation of the following form:

$$\alpha=a'\exp(b'[H^+]+c') \tag{31}$$

In this equation a', b', and c' are constants determined by minimizing the sum of the square of the weighted-relative error (SSWRE); the weights were determined by the number of experiments representing each of the calculated α values from the SSWRE equation. The weights were determined by the number of experiments representing each of the calculated α values; the result of this fit was:

$$\alpha=0.008092\exp(-371.272[H^+]-1.01692) \tag{32}$$

The final expression for the fraction of the calcium phosphate material remaining at time, t is:

$$\frac{M(t)}{M(30s)}=\exp\left[\alpha v_z^{0.70}(t-30)\right]. \tag{33}$$

Comparison of Theoretical Models to Experimental Data. The mass transfer model describes the molecular dissolution of calcium phosphate in a well defined flow field. In the dissolution based model, an important parameter in predicting the theoretical removal rate is the calcium phosphate solubility. In spite of the variation in the experimental solubility data, an attempt was made to assess how well the model predicted changes in experimental conditions. The scatter seen in experimental solubility studies required us to obtain a value for C_w derived from the dissolution model. C_w was obtained by finding the average slope of the fraction remaining versus time data generated in the decontamination experiments and calculating a C_w value that provided a similar slope. For example, at a pH of 2.85 the value of C_w was calculated to be 1.77 mg/mL. The dissolution model (Eq. 24) is compared to the decontamination rates for RO experiments having a solvent pH's of 2.85 and 3.24 and a flow rates ranging from 3.8 to 11.4 L/min (see Fig. 9). It can been seen that the region of applicability of the model is limited; the model slightly under predicts initial cleaning rates and over predicts cleaning rates over long periods of time. This deviation may be due to the rapid removal of calcium phosphate aggregates in the initial state of cleaning and the adhesion of residual deposits to the stainless steel at long times. These deviations could also be related to uncertainties in the coating thickness and variations in the quality of the water. Although there are variations, the model does show, the general trends in initial decontamination rates as a function of solvent flow rate and pH.

Many researchers have described cleaning processes in terms of the removal of large aggregates. Visual observation of the calcium phosphate films indicates that the surface of the film is nonuniform. Furthermore, the results reported here strongly suggest that the removal of the calcium phosphate is due to both residue dissolution and shearing of large chunks of the residues.

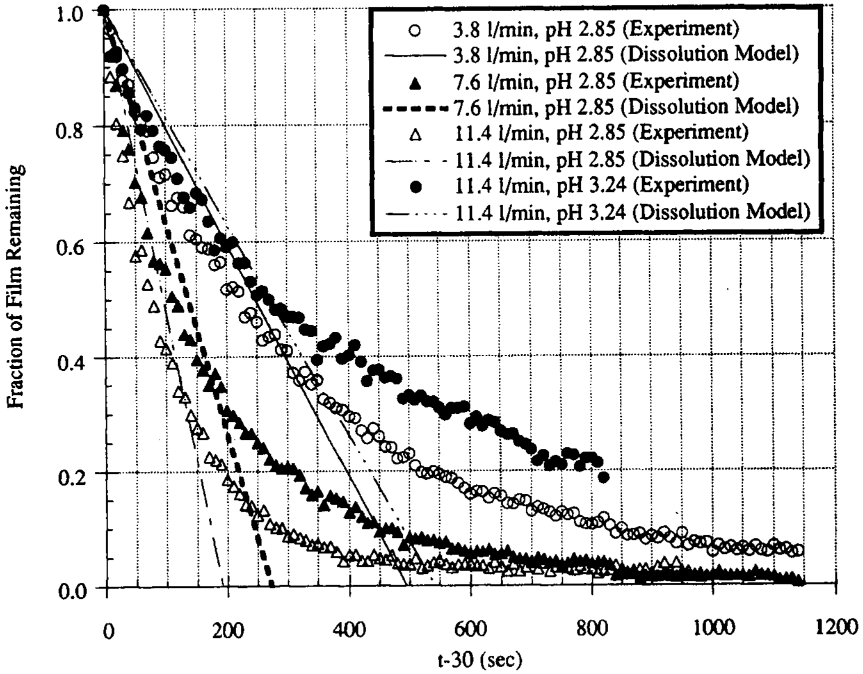

FIG. 9. COMPARISON OF DISSOLUTION MODEL (EQ. 24) TO DECONTAMINATION DATA FOR EXPERIMENTS PERFORMED AT A RANGE OF SOLVENT FLOW RATES (3.8-11.4 L/MIN) AND SOLVENT pHS (2.85-3.24)

Plots have been constructed to compare the modified first order model to the experimental data. The overall average error was determined by weighting the average errors according to the number of experiments performed at the different conditions. This error was found to be 6.70 for a pH range of 2.35 - 7.82 and a flow rate range of 3.8 to 11.4. Figure 10 compares the model empirical approximation (Eq. 33) with experimental runs at three solvent pH values and two flow rates. Although there are some deviations, the first order model predicts the removal of calcium phosphate relatively well; it captures the trends found with changing solvent flow rate and pH. Some of the deviations in the fit may be attributed to scatter in the original experimental data.

The application of a dissolution model versus the modified first-order model to a cleaning process can be discussed in terms of the velocity function. Kern and Seaton's model describing the removal of aggregates indicated that pure mechanical or shear based cleaning would result in a cleaning rate proportional to the amount of kinetic energy the solvent possessed (Kern 1959). They showed that cleaning from purely hydrodynamic effects (i.e., shear stress) would yield a cleaning rate with a velocity term to a power close to 2.0. In the modified first order model a cleaning rate proportional to the velocity to the 0.70 power suggests that the calcium phosphate/water system does not depend solely upon mechanical cleaning mechanisms. It appears that the dissolution model predicts the velocity trend more closely than that of a mechanical based cleaning model. However, the implementation of the model depends upon the accuracy of solubility measurements.

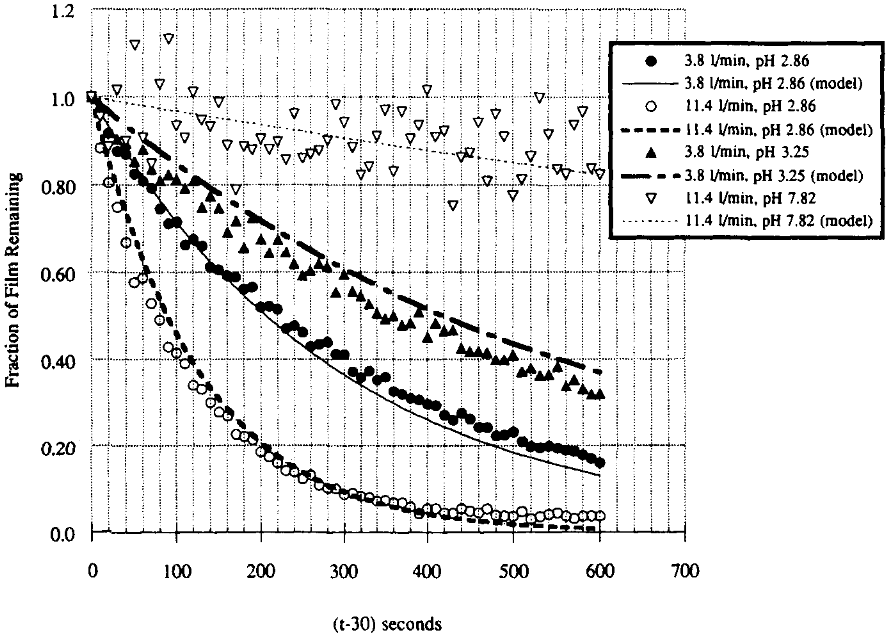

FIG. 10. COMPARISON OF MODIFIED FIRST ORDER MODEL (EQ. 33) TO EXPERIMENTS PERFORMED AT A RANGE OF pH AND FLOW RATES

Application of Calcium Phosphate Cleaning Studies to Protein Removal. The majority of industrial milk fouling is heterogeneous in nature. The next step in this research is a study of heterogeneous contaminants. Measuring real-time decontamination kinetics of these compounds may be done if a single component were radio-labeled and mixed with other unlabeled compounds. The observed cleaning mechanism for the removal of calcium phosphate is very different from studies on protein removal. In studies on the removal of milk deposits from stainless steel Jeurnink and Brinkman (1994) observed that the deposit is a spongy protein matrix with associated minerals and fat globules. In their study, the removal of the deposit with alkaline solutions proceeded by a two step mechanism. Initial contact with the alkaline solution caused the residue to swell and form cracks. Subsequent removal of the spongy, primarily protein layer was due to the shear stresses imparted by the cleaning solutions. The subsequent removal of the residual mineral layer was achieved using an acidic solution. The development of a model for protein removal similar to the modified first order model for calcium phosphate would require cleaning data as a function of velocity and alkali concentration. The application of this model could, however, be limited by the formation of a protein gel layer at high alkali concentrations (Jeurnink and Brinkman 1994).

The calcium deposit matrix often encountered during HTST processing is heterogeneous; it contains proteins and other milk components. The mineral residue that remains after removal of the other major components (e.g., protein via alkaline solutions) is often described as a hard, sandy deposit. The residues found in an actual processing facility are also created at a higher temperature; this may change the nature of the bonds formed between the residues and the stainless steel substrate. However, the Ca/P ratio of these deposits is approximated by our experimental conditions.

Because of the bonds that form during the development of the fouling residues from a bulk solution - the calcium phosphate films we developed will have a different chemical structure than an actual deposit. The removal of the spongy heterogeneous protein film by an alkali solution is often described in terms of both dissolution and spalling mechanisms. Spalling is the removal of large aggregates of material based on the breaking of bonds in the protein/mineral/fat residues. While the mechanism that we describe has these elements; it appears to be due primarily to the dissolution process.

There may be a difference in the mechanism and kinetics associated with the decontamination due to small differences in the solubility and the physical structure of the deposits. Although we do not have any direct experimental evidence, we are continuing to conduct experimental studies on the removal of mixed films (e.g., calcium phosphate and protein) from stainless steel surfaces using the solid scintillation technique.

CONCLUSIONS

SEM photographs of partially cleaned test coupons show that large aggregates of calcium phosphate are detached from the surface of test coupons during the cleaning process. This indicates that the calcium phosphate films are not removed solely by dissolution, but by a process that removed individual particles of calcium phosphate from the surface. It is believed that these particles are lifted from the hard surface by shear forces imparted by the fluid. This behavior is consistent with studies by Jeurnink and Brinkman (1994) on the spalling of milk deposits during the cleaning process.

In this project, our initial assumption was that the calcium phosphate would be removed solely through the process of dissolution. The flow of solvent past the solid residues was thought only to facilitate the removal of calcium phosphate by maintaining a concentration driving force for the dissolution process. The experimental data showed a large increase in decontamination rate with a decrease in solvent pH. The dissolution model based on the mass transfer of calcium phosphate predicted that if dissolution was the only film removal mechanism, the rate of removal would actually increase slightly over time because of the increase in surface area in contact with the solvent as layers of contaminant were removed. The decontamination data, however, showed that the rate of film removal did not increase over time, but instead showed a marked decrease.

The dissolution model also predicts the cleaning rate would be proportional to velocity raised to a power less than one. According to Kern and Seaton, if mechanical cleaning were the primary mechanism, the cleaning rate would be proportional to the kinetic energy of the fluid or the velocity to a power slightly less than two. Experiments have indicated that the cleaning rate is proportional to the velocity to the 0.70 power, suggesting that dissolution plays a significant role in the removal of calcium phosphate.

The dissolution based model, although theoretically sound, was difficult to test due to the absence of reliable solubility data. If, however, the solubility could be accurately determined, this model would still over predict the latter stages of calcium phosphate removal. The modified first order model developed in this work provided a more complete overview of the role of velocity and pH on the decontamination process.

An understanding of the mass transfer and hydrodynamic mechanisms governing the cleaning of contaminated surfaces is important in the development of efficient cleaning operations. This research has provided information on the mechanism of calcium phosphate removal by examining decontamination rates under various experimental conditions. It has also introduced a useful solid scintillation technique for noninvasively and continuously obtaining a measurement of the amount of material remaining on a solid surface. The accuracy of the decontamination experiments depends on the activity, uniformity and the initial mass and physical nature of the coating.

Many challenges still exist in the modeling of decontamination rates including the incorporation of surface morphology, effects of solvent additives (e.g., pH), the role of heterogeneous contaminants, and the geometry of the fouled surface into the models. The work presented here represents a first step to investigate the use of dissolution, shear stress and empirical based models to describe the removal of heterogeneous solid contaminants from stainless steel.

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NOMENCLATURE

Dimensions are given in terms of mass (M), length (L), time (t), and moles.

A	surface area of film, L^2.
a',b',c'	fitted dimensionless parameters (Eq. 31).
a, b, c	exponents in Eq. 26.
b_5	rate constant, M/t (see Table 1).
b_6	rate constant, 1/t (see Table 1).
C_b	bulk concentration of contaminant, moles/L^3.
$C_{OH,B}$	hydroxyl ion concentration in solvent, moles/L^3 (Eq. 4).
C_w	concentration of calcium phosphate at liquid - solid interface, moles/L^3.
C_x	concentration of contaminant to be removed, moles/L^3 (Eq. 4).
D_{soil}	diffusivity of film, L^2/t (Eq. 5).
g	gravitational acceleration, L/t^2.
J	molar flux @ liquid - solid interface, moles/tL^2.
k_m	effective mass transfer coefficient, L/t.
k	empirical rate constant, t^{-1}, (see Table 1); L^3/t moles (Eq. 4).
k_1	empirical rate constant, M/t (see Table 1).
L	length of mass transfer region, L.
M	mass of film, M.
M'	local mass, M.
M_0	initial mass of film, M.
$\bar{M}$	average molecular weight of film, M/moles.
N	moles of film, moles.
n	fitted dimensionless parameter (Eq. 30).
N(0)	number of incident beta particles (Eq. 1).
N(t')	number of particles transmitted through thickness t' (Eq. 1).
r_0	initial radius of liquid solid interface, L (Eq. 2).

R	radius of pipe, L.
Re	Reynolds number = $\frac{\rho v D}{\mu}$.
R_i	radius of film, L.
Sc	Schmidt number = $\frac{\mu}{\rho D_{AB}}$
Sh	Sherwood number = $\frac{kD}{D_{AB}}$
t	time, t.
t'	thickness of stainless steel window, L (Eq. 1).
t_{film}	thickness of film, L.
v	velocity of bulk solvent, L/t (Eq. 6).
$< v_z >$	average fluid velocity, L/t^2.
z	axial distance, L.
Z	dimensionless distance, $\frac{z}{L}$
z_w	thickness of film, L (Eq. 5).
x_{thick}	thickness of deposit, L

Greek Symbols

α	fitted parameter defined by Eq. 30, 31
β	dimensionless variable, $\beta=2\left[\frac{Sh}{ReSc}\right]\frac{L}{r_0}$ (Eq. 21)
η	dimensionless time, $\eta = t < v_z > /L$ (Eq. 15).
κ	dimensionless variable, $\kappa=\frac{\bar{M}C_w}{2r_0}(1-e^{-\beta})$ (Eq. 25).
ϕ	dimensionless radius, $\frac{R_i}{r_0}$ (Eq. 12)
$\bar{\phi}$	average dimensionless radius
μ_m	mass absorption coefficient, L^2/M (Eq. 1).
μ	viscosity, M/L t.
ρ	density of solvent, M/L^3.
ρo	density of film, M/L^3 (Eq. 2).
Θ	C_b - C_w, concentration gradient, moles/L^3.
τ	shear stress, M/t^2L (see Table 1).

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