

*2003 ECI Conference on Heat Exchanger Fouling and
Cleaning: Fundamentals and Applications*

Santa Fe, New Mexico, USA

Editors: Paul Watkinson, Hans Müller-Steinhagen, and M. Reza Malayeri

Year 2004

Paper 16

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Calcium Phosphate on Modified Stainless Steel

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<http://services.bepress.com/eci/heatexchanger/16>

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Abstract

In order to reduce the fouling caused by milk during heat treatment, it is important to know more about the deposition process of calcium phosphate, one of the main components of milk fouling, on stainless steel surfaces. The fouling behaviour of calcium phosphate is controlled by several factors related to both the fouling solution properties and the surface characteristics. The present work is focused on the influence of two of these factors: 1) the size and size distribution of the calcium phosphate aggregates formed in solution upon heating and 2) the surface tension values of the deposition surface. It was possible to conclude that maximum deposit build up occurs at the temperature corresponding to the formation, in the bulk, of amorphous sphere-like calcium phosphate particles of about 0.1mm diameter and considering the surface effect, the maximum deposition is obtained on those surfaces having higher surface tension values.

STUDY OF THE INFLUENCE OF BULK PROPERTIES AND SURFACE TENSION ON THE DEPOSITION PROCESS OF CALCIUM PHOSPHATE ON MODIFIED STAINLESS STEEL

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ABSTRACT

In order to reduce the fouling caused by milk during heat treatment, it is important to know more about the deposition process of calcium phosphate, one of the main components of milk fouling, on stainless steel surfaces.

The fouling behaviour of calcium phosphate is controlled by several factors related to both the fouling solution properties and the surface characteristics. The present work is focused on the influence of two of these factors: 1) the size and size distribution of the calcium phosphate aggregates formed in solution upon heating and 2) the surface tension values of the deposition surface.

It was possible to conclude that maximum deposit build up occurs at the temperature corresponding to the formation, in the bulk, of amorphous sphere-like calcium phosphate particles of about 0.1 μ m diameter and considering the surface effect, the maximum deposition is obtained on those surfaces having higher surface tension values.

INTRODUCTION

Fouling of processing equipment in the dairy industry has been one of the main challenges for researchers within food engineering. The present work is focused on fouling caused by milk during heat treatment, more precisely on the fouling behaviour of calcium phosphate, the main mineral component of milk deposits (Jeurnink *et al.*, 1996; Visser, 1999).

Calcium phosphate deposition and adhesion on a solid surface is a result of a competition between different types of interactions involving the calcium phosphate particles, the deposition surface, the solvent and any other solute present in the system. The challenge in this work is to determine the influence of some of these factors on the amount of calcium phosphate deposition.

The calcium phosphate deposition mechanism can be divided into several steps where all the factors can be included. The process starts with calcium phosphate particle formation in the bulk upon heating. Calcium and phosphate ions that are normally present in ionic or sub-colloidal form, start forming a colloidal calcium phosphate complex. As

postulated (Visser, 1997), the formation of these calcium phosphate complexes starts with the formation of amorphous calcium phosphate (ACP), which is subsequently transformed via octa-calcium phosphate (OCP) to hydroxyapatite (HAP), the most thermodynamically stable form of calcium phosphate. This complex formation is detected by an increase in solution turbidity, which seems to indicate that particle formation occurs in the bulk liquid. These foulant particles as well as the other ionic species present in solution are then transported to the heated surface. Once at the vicinity of the surface, they can adhere to it following a process that is dependent on the forces established between the foulants and the surface. The latter is considered to be the controlling step for the whole process and dependent on the surface characteristics of the metal support, the surface properties of the particles and the physico-chemical interaction forces between them. The forces that play a role in the adhesion of the calcium phosphate onto a metal heated surface are, according to van Oss (1994), the Lifshitz- Van der Waals interaction forces (LW), the electrostatic double layer interaction forces (EL), the Lewis acid/base interaction forces (AB) and the Brownian motion (Br). As a result of all of these forces, van Oss divided the surface tension of a surface into four components, the electron donor (γ^- component) being the most often used characterizing component for solid surfaces (Rosmaninho *et al.*, 2001; van Oss *et al.*, 1997, Wu and Nancollas, 1998).

After the first layer is formed on the solid surface, other particles coming from the bulk liquid adhere on top of this layer and develop a structured deposit. The structure of this deposit depends on both the structure of the first layer, which depends mainly on the surface properties, and on the particles and ions present in solution. The process at the surface thus involves, not only particle attachment but also particle growth.

In time, the deposit develops into a more consolidated and stable structure.

MATERIAL AND METHODS

Bulk Characterization

Calcium Phosphate: Calcium phosphate deposition was performed using SMUF (Simulated Milk Ultra Filtrate), which is a water solution that simulates the mineral composition of milk. It was prepared according to Jenness and Koops (1962), pH value adjusted to 6.70 with NaOH 0.5M and kept overnight at 5°C before use.

Particle Size Characterization: The size of the calcium phosphate particles formed in the bulk upon heating was determined with the help of a Coulter Counter Analyser (Coulter LS230).

After being heated to the desired temperature, the solution was vacuum filtered and the deposit obtained was dried. This deposit was afterwards suspended in ethanol and analysed using the Coulter Counter.

The analysis was based on the distribution of the number of particles detected. Each data point represents the mean value of two measurements.

Turbidity Measurements: Particle formation in the bulk can be detected by the increase in the turbidity of the SMUF solution. Turbidity measurements during heating were done using a UV/VIS Spectrophotometer (Philips PU8620) at a wavelength of 610 nm.

Morphological Characterization: The type of calcium phosphate structures formed was observed by scanning electron microscopy (JEOL JSM6301F).

Surface Characterization

Stainless Steel Surfaces: To study the influence of the surface tension of the support on the deposition process, different surfaces with a wide range of surface tension and similar roughness were used.

All surfaces were 316 2R (bright annealed) based and suffered four types of surface modification processes in order to change their surface tension:

- Ion implantation: SiF_3^+ and MoS_2 ions were implanted in the surface by ion bombardment in a depth of approximately 0,2 μm ;
- Coating by Plasma CVD (Chemical Vapor Deposition): SiO_x and DLC-Si-O;
- Ni-P-PTFE coating: autocatalytic fixing of PTFE particles in a Ni-P matrix with a proportion of about 30% PTFE;
- Silica coating obtained by a sol-gel process.

Cleaning Procedures: Before each deposition experiment as well as before the determination of the surface tension of each sample, all stainless steel samples were cleaned with a commercial detergent (RBS35 from RBS Chemical Products) according to the following procedure: 1) samples were immersed in a 2.0% w/v detergent (RBS35) solution in distilled water at 65°C for 5 min.; 2) rinsed with distilled water at 65 °C for 5 min. and 3) rinsed with distilled water at 20°C.

Contact Angle Measurements: Contact angle values were measured by the sessile drop method in a contact angle meter (DataPhysics OCA15 Plus) using water, formamide and α -bromonaphtalene (α -BR) as reference liquids. The contact angles were measured automatically using an image analyzing system. Contact angle measurements were performed on every stainless steel sample 24h after being cleaned.

Surface Tension Determination: Through contact angle measurements and using the approach of van Oss (1994) it is possible to evaluate the surface characteristics of a solid in terms of its surface tension (γ_s). This approach considers the total surface tension of a solid or a liquid (γ^{TOT}) as the sum of an apolar Lifshitz-van der Waals component (γ^{LW}) and an acid-base polar component (γ^{AB}):

$$\gamma^{TOT} = \gamma^{LW} + \gamma^{AB} \quad (1)$$

Lifshitz-van der Waals interactions arise due to three distinct interactions, induction (Debye), orientation (Keesom) and dispersion (London) the last one being the most significant term (van Oss, 1994).

The acid-base forces are always asymmetric since they comprise the electron donating as well as the electron accepting properties of a surface. Thus the acid base component (γ^{AB}) consists of two non-additive parameters, one for the electron donor (γ^+) and one for the electron acceptor (γ^-) contribution (van Oss, 1994).

$$\gamma^{AB} = 2\sqrt{\gamma^+ \gamma^-} \quad (2)$$

The total interfacial tension between phases i and j can be expressed as

$$\gamma_{ij}^{TOT} = \gamma_i^{LW} + \gamma_j^{LW} - 2\sqrt{\gamma_i^{LW} \gamma_j^{LW}} + 2\left(\sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_j^+ \gamma_i^-} - \sqrt{\gamma_i^+ \gamma_j^-} - \sqrt{\gamma_i^- \gamma_j^+}\right) \quad (3)$$

Contact angle values (θ) can be related to the total interfacial tension using simultaneously three forms of the following equation resulting from Young's equation, one for each reference liquid used

$$(1 + \cos \Theta) \gamma_l^{TOT} = 2\left(\sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+}\right) \quad (4)$$

where subscripts s and l mean solid and liquid, respectively.

Experimental Equipment and Conditions

Rotating Disk Apparatus: The rotating disk apparatus (Figure 1) was used to study the deposition of calcium phosphate onto a surface under controlled hydrodynamics. The apparatus is composed of a hollow cone containing heated silicone oil that can freely rotate in the SMUF solution. The solution is contained in a cylindrical

thermostatted vessel whose temperature can be adjusted. The stainless steel sample used as deposition support is attached to the bottom of the heated cone by using a double-sided tape.

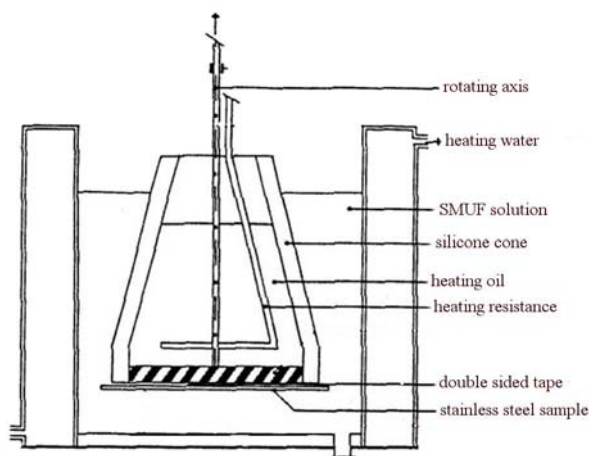


Figure 1: Scheme of rotating disk apparatus

Experimental Conditions: The aim of these experiments was to simulate the heating behaviour of a solution in a heat exchanger channel and therefore the deposition of calcium phosphate was evaluated at increasing temperatures from 40 to 75°C.

SMUF solution was introduced in the thermostatted vessel of the rotating disk apparatus and its temperature was initially adjusted to 40 °C. When that temperature was reached, the stainless steel sample (90 mm in diameter) was attached to the silicone cone previously heated and submerged in the solution. The sample was kept rotating at a speed of 250 rpm (turbulent regime, Reynolds number between 8.8×10^4 and 12.8×10^4 for 40 and 75°C respectively) for 10 min., lifted from the solution, detached from the cone, dried up in air and weighed to evaluate the amount of deposit formed.

The solution was then heated to 43°C and when that temperature had been reached, the whole process was repeated using a new sample.

The subsequent temperatures were 45, 48, 50, 60 and 75°C and the same temperature difference (70°C) between the solution and the heated cone was kept.

A new SMUF solution was then prepared and the whole process was repeated, using the same stainless steel sample for each temperature.

As a total, three SMUF solutions were used and so 30 min. deposition experiments were made for each temperature (and sample). Both the temperature and the pH (WTW inolab pH level1) of the solution were followed over time in order to better characterize bulk behaviour.

Deposit: The amount of deposit formed on each sample was determined by weighing the samples before and after the deposition using an analytical balance (AND GR-200).

RESULTS

Surface Characterisation by Contact Angle Analysis

To evaluate the influence of the deposition support on calcium phosphate deposition process, several stainless steel based surfaces with different surface properties were tested. The surfaces were obtained by different surface modification techniques that were able to change their surface tension values while keeping similar roughness properties. The different stainless steel surfaces can then be distinguished by their surface tension values (Table 1), which were determined by contact angle measurements and calculated according to equation (4).

Table 1 Surface tension components for all the stainless steel samples analysed (standard deviation in brackets)

Surface	γ^{LW}	γ^+	γ^-	γ^{TOT}
Modifications	(mJ/m ²)	(mJ/m ²)	(mJ/m ²)	(mJ/m ²)
Unmodified	38.7 (0.1)	1.4 (0.1)	39.1 (3.1)	53.4 (0.2)
DLC-Si-O	42.9 (0.4)	1.6 (1.0)	15.0 (3.2)	52.7 (1.3)
MoS ₂	38.3 (0.1)	0.7 (0.2)	20.4 (4.1)	45.7 (1.8)
Silica	36.2 (0.7)	1.1 (0.2)	14.8 (1.5)	44.3 (1.7)
SiF ₃ ⁺	37.1 (1.0)	1.1 (0.7)	36.8 (0.6)	49.8 (3.5)
SiO _x	34.8 (4.4)	1.1 (0.5)	53.3 (1.2)	49.8 (8.2)
Ni-P-PTFE	18.1 (2.0)	0.1 (0.2)	2.2 (0.6)	19.1 (2.8)

According to van Oss (1994) and the Lewis acid-base theory, surface tension can be divided into three components, the Lifshitz-van der Waals component (γ^{LW}), the acid-base component that can be divided into an electron acceptor (γ^+), an electron donor component (γ^-) and total component resulting from the other three (γ^{TOT}). The most distinguishing factor among surfaces is the electron donor component (γ^-) and therefore that will be the characterizing factor considered along this work. The use of this factor also permits to cover a wide range of surface tension values, resulting in better surface tension dependence for the deposition process.

Deposition Process Dependence on Temperature

By plotting the amount of deposit obtained against the deposition temperature it is possible to simulate a deposition profile along the heat exchanger (Figure 2).

Each deposition stage ("dep" in the legend) refers to a 10 minutes deposition at a constant temperature at a rotating speed of 250 rpm. For all three depositions, the profile showed a dependence on temperature. Instead of an increasing relation with temperature, a maximum deposition value was obtained at 45°C for each stage.

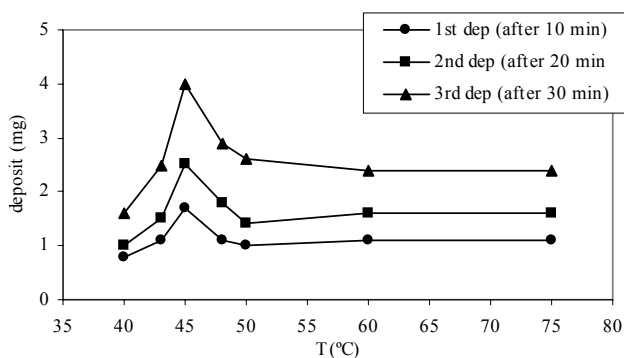


Figure 2 Deposition profile along a heat exchanger (amount of deposit obtained for the three sequential depositions on MoS₂ 2R samples, for the whole range of temperatures tested)

The temperature profile obtained after the first 10 minutes (first deposition layer) was kept during the subsequent deposition stages, indicating that surface-calcium phosphate interactions play an important role in the process.

On the other hand, temperature dependence of the process seemed to be related to bulk properties or bulk properties change with heating, requiring an insight in bulk characterization.

Bulk and Bulk Particles Characterization

Upon heating, supersaturation according to calcium phosphate can be achieved and bulk precipitation starts to occur. This fact can be verified by the increase in bulk turbidity. In order to know the temperature at which bulk precipitation starts, the heating of SMUF solution was followed by spectroscopy at 610 nm (Figure 3).

Solution stayed clear until the temperature of 45° was reached. This indicates that at the temperature of maximum deposition referred to previously (Figure 2) correspond the beginning of bulk precipitation.

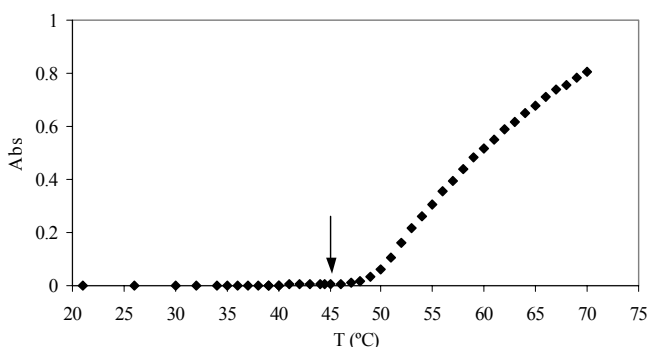


Figure 3 Turbidity evolution of SMUF solution with temperature (λ 610 nm)

The turbidity increase in time can be caused by either the enlargement of the particles already formed in the bulk or by the increase in the number of particles present. To

better evaluate which phenomenon was happening, the size of the particles formed for each temperature was also evaluated (Figure 4). The particles formed in solution during heating were filtered, dried and analysed in Coulter Counter equipment after being dispersed in an ethanol solution. Although it is also possible that the number of particles is rising with heating, it can also be confirmed that particles grow to about four times their initial size (from particles of about 0.1 μ m diameter to particles of about 0.4 μ m) from a temperature of 45°C to a temperature of 70°C.

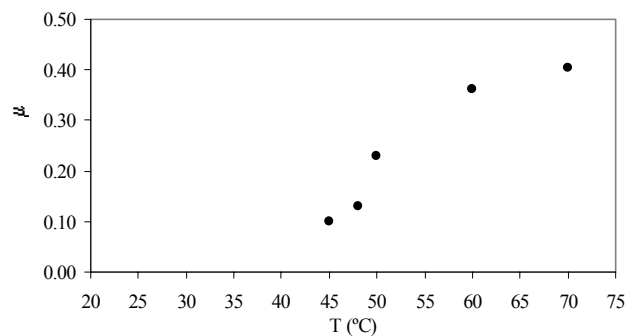


Figure 4 Evolution of calcium phosphate particle size with heating

Despite the particle size being an important factor for the process, the deposition behaviour may not be only dependent on the size of the particles present in solution but also on their structure, composition and degree of crystallinity. For a deeper structural characterization, the deposits obtained at the different temperatures were then analysed by other techniques.

As confirmed by X-ray microanalysis (Noran Voyager), all the particles formed, independent of their size and temperature of formation, were calcium phosphate. According to the pictures obtained by scanning electron microscopy (SEM) they all had a sphere-like structure, characteristic of hydroxyapatite compounds (Kemenade and Bruyn, 1987; Visser and Jeurnink, 1997).

Figures 5 and 6 show differences according to particle size, the similarity according to the sphere like structure as well as the differences in the compactness of the agglomerates. Precipitates obtained at 45°C, which are the first structures detected in the bulk, are small, aggregated in a very compact grapelike form (Figure 5b) and show a lamellar form at a macromolecular level (Figure 5a). At the other end of the temperature scale, deposits formed at 70°C are composed of bigger particles that tend to aggregate in a more loose form (Figure 6b). This last type of deposit has a powder-like aspect that easily spreads on the surface (Figure 6a).

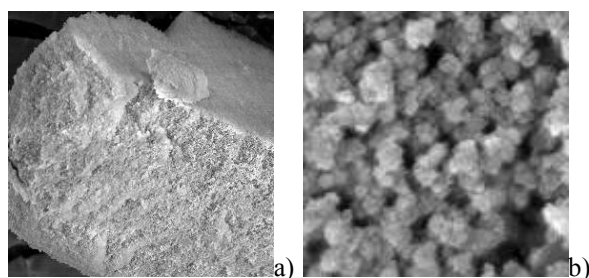


Figure 5 SEM images of calcium phosphate formed in the bulk at 45°C a) agglomerates (1000x); b) type of structure (20000x)

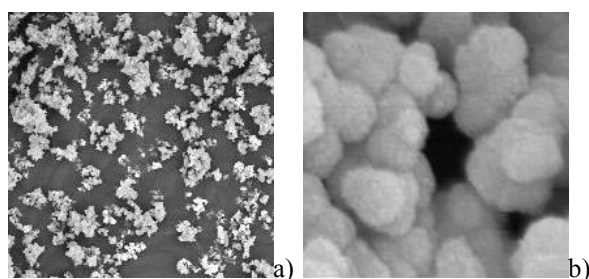


Figure 6 SEM images of calcium phosphate formed in the bulk at 70°C a) agglomerates (1000x); b) type of structure (20000x)

Opposed to the lamellar forms (45°C) that proved to be totally amorphous when analysed by x-ray diffraction, these powder-like forms (70°C) show some degree of crystallinity.

Considering bulk properties and comparing the different types of structures formed as a function of temperature, calcium phosphate maximum deposition is achieved for amorphous small diameter particles.

Surface Properties

The deposition process also involves the deposition support, which was also tested for its role. To do so, calcium phosphate deposition was performed on the different surfaces presented earlier. The same kind of temperature dependence presented in Figure 2 was found for all the surfaces analysed, having a maximum deposition at a temperature of 45°C. Evaluation of the influence of the surface on the process can be done by plotting the maximum amount of deposit formed for each sample during a total period of 30 min., against the electron donor (γ^-) component of its surface tension (Figure 7). From the data on Figure 7 it is possible to conclude that:

- 1) maximum amount of deposit obtained depends on the support chosen;
- 2) surfaces having higher γ^- component values are more prone to calcium phosphate deposition or at least they allow more deposit formation. When changing from a surface with a γ^- of 1 mJ/m² to a surface with about 50 mJ/m², the amount of calcium phosphate deposit increases about 5 times.

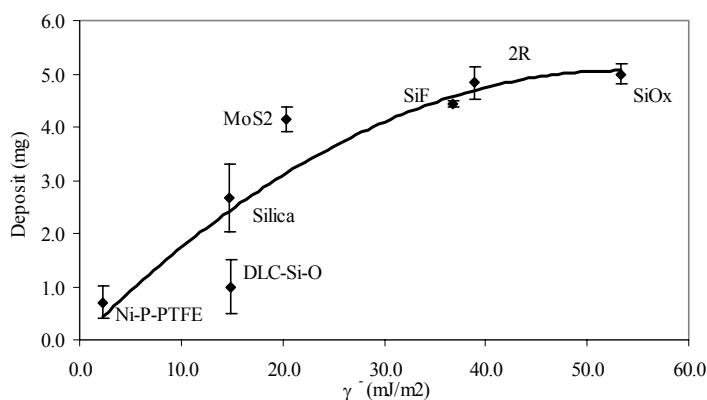


Figure 7 Dependence of the amount of deposit obtained on the surface tension of the support

CONCLUSIONS

The deposition process of calcium phosphate on stainless steel surfaces depends on two different types of factors:

- 1) bulk properties, more precisely the size of calcium phosphate particles formed, the type of agglomerates these particles form and their crystallinity degree; Maximum deposit formation can be found for the first type of structures formed in the bulk upon heating which are smaller, amorphous and tend to aggregate into a more compact structure.
- 2) surface properties as the surface tension value of the deposition support. Maximum deposition is obtained for surfaces having higher values for the electron donor (γ^-) component of surface tension.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the MODSTEEL Project (The European Commission, DG Research, Growth Programme, Contract nr. G5RD-CT-1999-00066) and “Fundação Luso-Americana para o Desenvolvimento” (FLAD). The authors also acknowledge Professor Alexandra Pinto for the use of the Coulter Counter.

NOMENCLATURE

SMUF	Simulated Milk Ultra Filtrate
DLC	Diamond like carbon
Ni-P-PTFE	Nickel-Phosphor-Poly-Tetrafluorethylene
γ	Surface tension [mJ/m ²]
γ^{LW}	Lifshitz-van der Waals component [mJ/m ²]
γ^{AB}	Acid-base component [mJ/m ²]
γ^-	Electron donor [mJ/m ²]
γ^+	Electron acceptor [mJ/m ²]
θ	contact angle values [°]

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