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Using Nature to Provide Solutions to Calcareous Scale Deposition

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Abstract

The field of biomimetics is expanding in engineering and refers to the mimicking of natural system functionality in technological systems. The most well known example of biomimetics is the development of Velcro which resulted from the inability of burrs from bushes to be removed from the fur of a dog. Biomimetics in surface engineering is also receiving attention as nature provides surfaces with a whole range of functionality. This is often achieved by nanostructuring at different length scales. This work is an initial study of some nanostructured polymer surfaces, derived from the anti-reflective moth-eye structure as surfaces to reduce mineral scale deposition. The study has shown that compared to stainless steel the polymer surfaces all reduce scale deposition and also within the polymers there is a range of behaviour. Some initial suggestions of the controlling factors in deposition on these systems are discussed.

Introduction

There are many approaches to remove and prevent scaling with chemical inhibition, chemical scale removers and mechanical methods being the most prevalent ones. Chemical scale removers tend to be more inexpensive and can reach where mechanical methods cannot. For example, carbonate scales can be removed by hydrochloric acid, however, the acid reaction tends to produce spent acid that may promote the reformation of scale later on. Sulphate scales can be removed by strong chelating agents such as EDTA. However, the reactivity in such approaches can be too slow to make it an effective method thus there is also the additional use of solvents and preflushes.

Chemical inhibition usually involves phosphate compounds, inorganic polyphosphates, organic aminophosphates and organic polymers. They range from the basic dilution method to the most advanced and economical of threshold scale inhibitors (N. Abdel-Aal and K. Sawada 2003; Evangelos Dalas and Petros G. Koutsoukos 1990; Jasber S. Gill 1999; Granit N. Filip, Korin E. and Bettelheim A. 2003; Mahmut Parlaktuna and Ender Okandan 1989; Q. F. Yang, Y. Liu, Anzhong Gu, J. Ding and Ziqiu Shen 2002). Due to recent environmental awareness, there is a call for chemical inhibitors to go environmentally acceptable and less toxic to the environment, thus the development of green inhibitors.

In some instances scale control at surfaces may be addressed by surface engineering options. In biofouling there have been enormous efforts to reduce deposition of marine biological species on surfaces by some really sophisticated surface engineering systems which can release anti-fouling agents at a controlled rate, can decrease the surface roughness and various other mechanisms (A. Barrios Carlos, Xu Qingwei, Cutright Teresa and Newby Bi-min Zhang 2004; Bretagnol Frederic, Lejeune Michael, Papadopoulou-Bourauoi Andri et al. 2005; Y. Hanein, Y. Vickie Pan, B. D. Ratner, D. D. Denton and K. F. Bohringer 2001; L. Dalsin Jeffrey and B. Messersmith Phillip 2005; Perez Miriam, Blustein Guillermo, Garcia Monica, del Amo Beatriz and Stupak Mirta 2005; N.A. Ochoa, M. Masuelli and J. Marchese 2005). In scaling there have been a few attempts at using surface engineering to control scale deposition, especially in the desalination industry, but it is fair to say that there is potential for more widespread study and exploitation of potential systems.

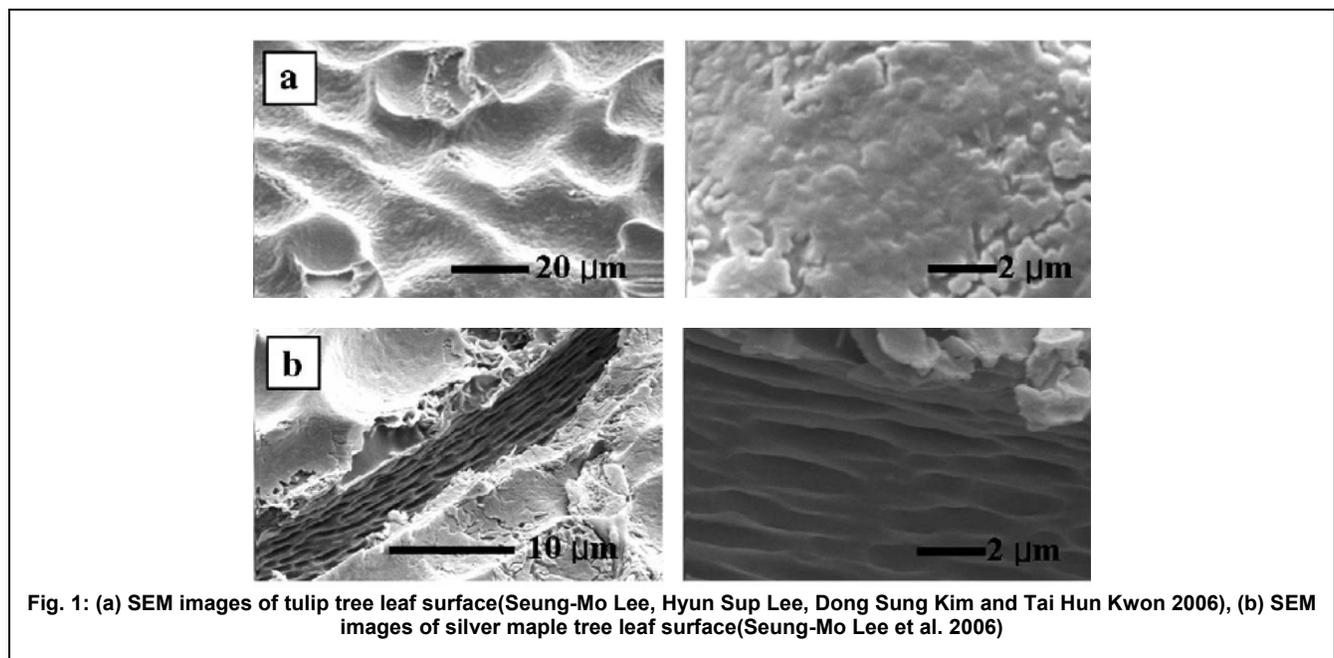
It has been shown that fouling adhesion is lower and prolong induction times (M. Forster and W. Augustin 1999; Q. F. Yang, D. Q. Xu and Z. Q. Shen 1994) in systems that have low surface energies (H. Muller-Steinhagen and Q. Zhao 1997; R. H. Rankin and W. L. Adamson 1973). Surface energy on metal surfaces can be reduced with ion implantation whereby elements with weak metal properties e.g. F, C, H, Si, etc are implanted onto a metal surfaces causing the number of free electrons on the surface to decrease. In the experiment carried out by Müller-Steinhagen and Zhao (Antje Bornhorst, H. Muller-Steinhagen

and Qi Zhao 1999), the CaSO_4 scale on an implanted stainless steel surface compared to a bare one was comparably more loose and porous which can be broken and washed away more easily. Roques and Girou(H. Roques and A. Girou 1974) measured periods of supersaturated CaCO_3 solutions held in cells of different materials and found that the induction periods were lowest for polished stainless steel and highest for PVC which had the lower surface energy.

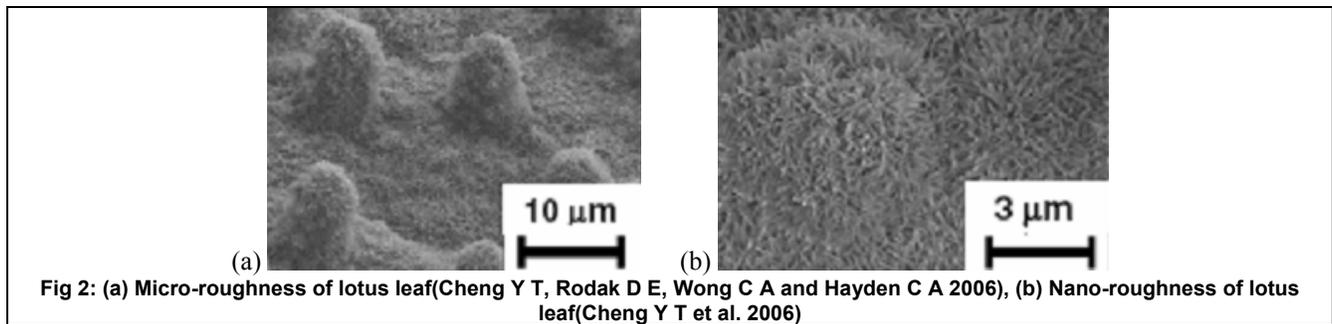
Surface energy can also be reduced by ion-sputtered diamond like carbon(M. Forster and W. Augustin 1999), self-assembled monolayers (SAMS)(Q. F. Yang, J. Ding and Z. Q. Shen 2000), electroless plating surfaces(Q. F. Yang, J. Ding and Z. Q. Shen 2000b) and ion implant nitrogen(Q. F. Yang et al. 1994). Polytetrafluoroethylene (PTFE) exhibits a very high melting point and low surface energy – 18.6mN/m , consequently Ni-P-PTFE composite films possess high stability and low surface energy(J. S. Hadley and L. E. Harland 1987; M. Nishira and O. Takano 1994). A graded electroless Ni-Cu-PTFE composite coating applied on heat transfer surfaces was also found to inhibit the formation of CaSO_4 scale significantly due to its non-stick and corrosion resistant properties(Q. Zhao and Y. Liu 2004; Q. Zhao, Y. Liu, C. Wang, S. Wang and H. Müller-Steinhagen 2005). Diamond-like carbon (DLC) coatings with their chemical inertness, high wear and corrosion resistance, good thermal conductivity and adhesion to metal substrate have been successfully applied in many industries. Fluorinated DLC coatings with an optimal surface energy have also been found to reduce scale adhesion significantly(Q. Zhao and X. Wang 2004).

In addition to surface energy, other surface properties, including coating morphology or roughness, and surface charge have significant influence on scale formation and its microstructure. Most real surfaces have roughness on many different length scales, ranging from the macro to the molecular. Normally, each unit area of substrate has a finite number of nucleation active sites and the probability of nucleation depends on the number of free sites. Surface material such as adsorptivity, charge and corrosiveness are surface properties that affect scaling. On the other hand, if the surface presents a microroughness, the minimal number of contact points may reduce the possibility of adhesion since it reduces the contact area between the bodies(B. J. Briscoe and S. S. Panesar 1992; H. Krupp 1967; R. Oliveira 1997; D. Tabor 1977). Surfaces may possess a roughness in several length scales, but due to short range of the van der Waals interaction, roughness in nanoscale ultimately determines the strength of adhesion(J. Katainen, M. Paajanen, E. Ahtola, V. Pore and J. Lahtinen 2006).

Nature provides many extremely interesting surface microstructures and in this study one is chosen which has anti-reflective properties; the moth eye. These are described later but Figure 1 gives some examples of other surfaces which have roughness on different length scales.



There has been much interest in the surface of the Lotus leaf which has a dual scale roughness as shown in Figure 2. It has extremely good self-cleaning properties which are as a result of the forces generated between the adherent and the microstructure and the ability of air to be trapped in that microstructure. The surface exhibits superhydrophobic properties and because droplets can roll off easily it is often referred to as a self-cleaning surface as any deposited dirt is swept away by the droplets which form very high contact angle with the surface.



This study is a very preliminary look at polymer surfaces with different nanostructures and to assess their ability to control CaCO_3 scale formation. It opens up a wide area of study which ultimately could lead to surface compositions, nanoscale roughness and chemistries being prescribed which will give optimum reduction in deposition and reduced adhesion of scale.

Experimental Methods

Reagents

To create the supersaturated solutions for this study, calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$), sodium chloride (NaCl), sodium bicarbonate (NaHCO_3) of analytical grade supplied by BDH Laboratory were used. The solutions were made using distilled water.

Table 1: Composition of the solutions (Brine 1, Brine 2) used in this study

	Brine 1 (mg/L)	Brine 2 (mg/L)
NaCl	15, 367	15, 367
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	15, 743	-
NaHCO_3	-	6, 046

Experiments were carried out in a 1 litre vessel thermostated at 70°C . 1000-ml scale formation solution was used in each experiment. CaCO_3 was precipitated spontaneously by mixing two solutions (500 ml brine 1 containing calcium ions and 500 ml brine 2 containing bicarbonate ions). Before mixing, the two solutions were filtered using a $0.2\mu\text{m}$ filter and subsequently heated up to 70°C in a water bath and buffered to pH of 6.8 by bubbling CO_2 gas and adding NaOH solution. The pH of the experiment was kept constant at 6.8 throughout.

Composition of substrates

Different polymer surfaces and a reference stainless steel sample were used as the substrates onto which CaCO_3 scale was deposited. Each polymer sample was wrapped around a stainless steel rotating cylinder electrode that was then rotated at 1800 rpm for an hour. The weight of each sample before and after the experiment was measured.

The LEO 1530 Gemini FEGSEM (Scanning electron microscope) with Oxford Instruments 350 EDX system was then used to analyze the scale coverage and scale morphology after the experiment. This instrument possesses high resolution, low kV, secondary electron imaging plus EBSD/EDX capabilities. The stainless steel and polymer surfaces had to be coated with a layer of conductive material, in this case it was sputter coated with Pt/Pd (platinum) of 3nm thickness. The coating also improves contrast in addition to increasing its conductivity.

SEM images of the polymers can be seen in Figure 3.

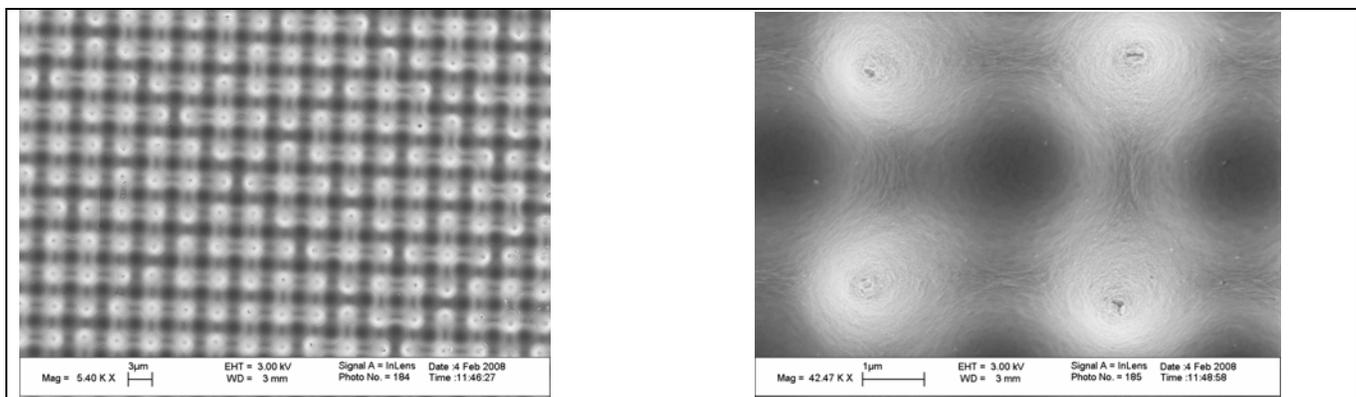


Fig. 3(a) L4693: Micro-mounds are roughly 3 μ m apart from each other.

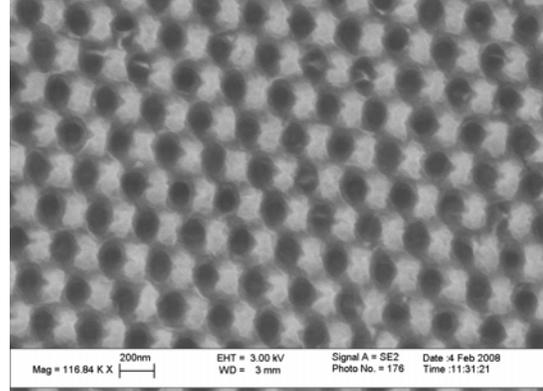
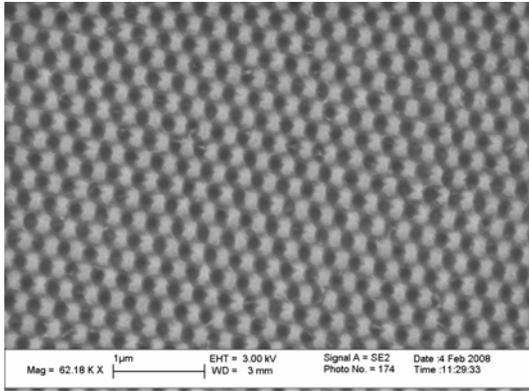


Fig.3(b) S – Standard: Nanostructures are roughly 250nm apart from each other and arranged in a hexagonal manner.

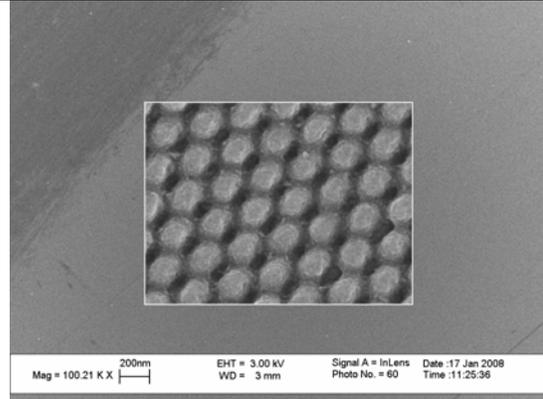
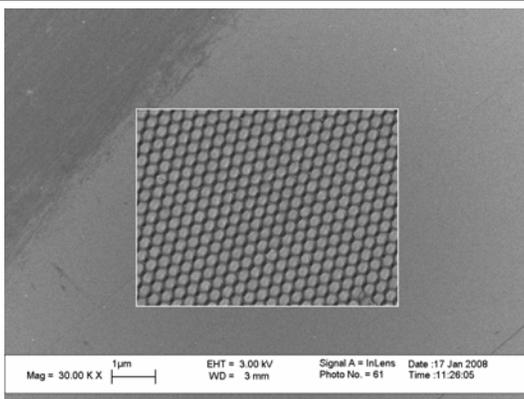


Fig.3(c) K: Nanostructures are roughly 250nm apart from each other and arranged in a hexagonal manner.

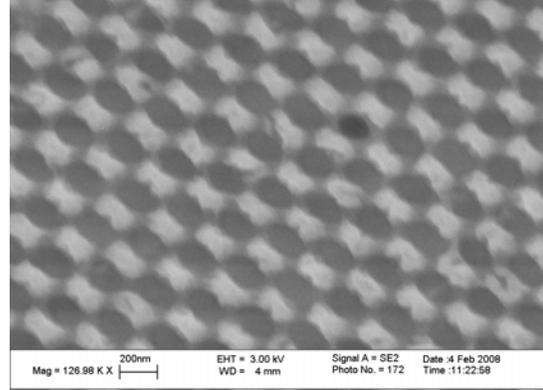
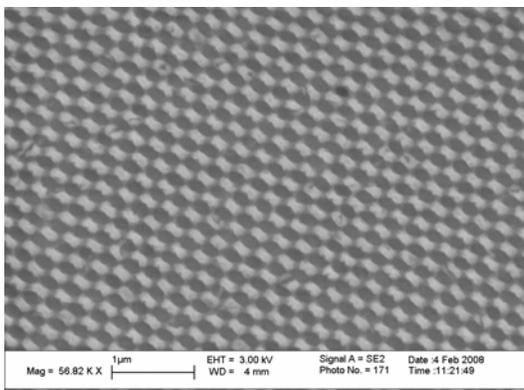


Fig.3(d) S – Fluoro: Nanostructures are regularly arranged and roughly 250nm apart from each other.

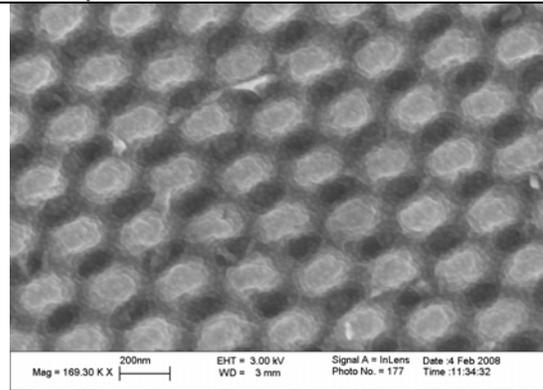
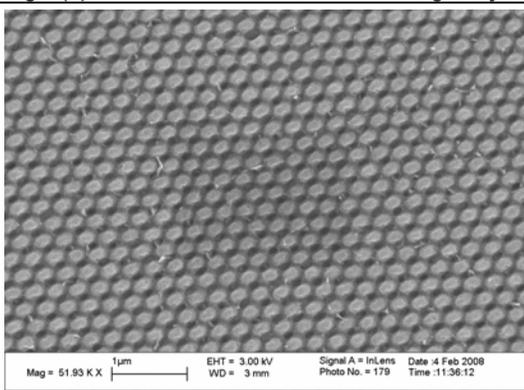


Fig. 3(e) S – Nano: Nanostructures are regularly arranged and roughly 250nm apart from each other. Each structure possesses a further roughness of its own due to tinier mounds covering its surface.

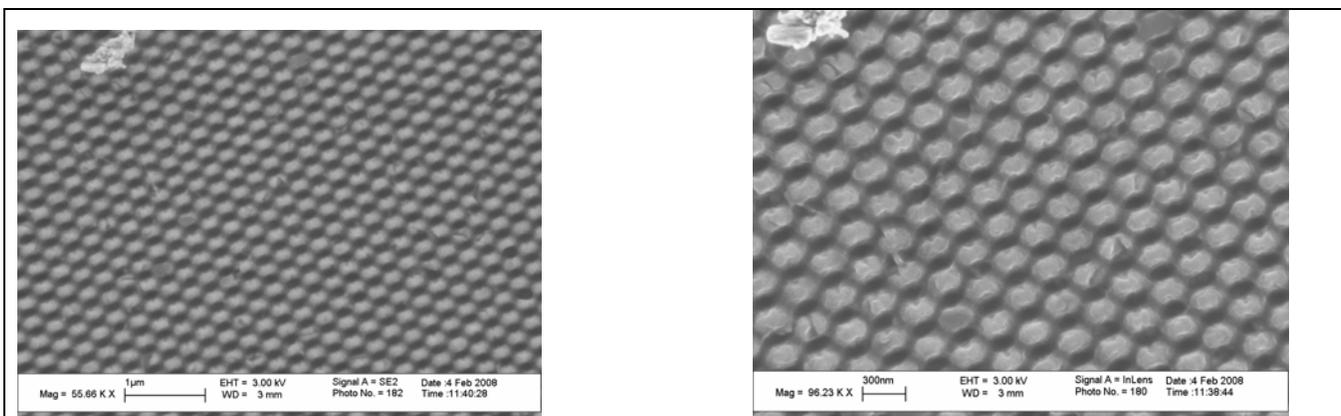


Fig. 3(f) S – Silicone: Nanostructures are regularly arranged and roughly 250nm apart from each other.

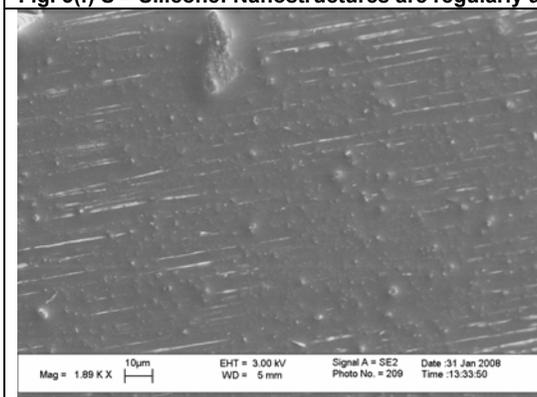


Fig. 3(g) Stainless Steel

Figure 3: SEM images of substrates used in this study.

Polymer surfaces used in this study

All samples were prepared using MacDermid Autotype’s PNR process (Precision Nano Replication) which on a roll-to-roll basis presses a sheet of nickel containing the required nanostructure into a coating of a UV-curable material on polyester. Once in contact, UV light is shone through the polyester, curing the material which is then released from the nickel sheet. This gives faithful replication of nano-scaled high aspect-ratio structures such as the motheye structures used in these tests. Special treatments are provided to ensure that the UV-curing material has high adhesion to the polyester film.

In these tests, the following range of UV-curable materials was used.

- S – Standard A typical UV-curable acrylate system
- S – Fluoro Standard + fluoro-molecules for lower surface energy
- S - Nano Standard system containing silica nanoparticles
- S - Silicone A UV curable silicone system with lower surface energy
- K Nanoparticle formulation on a deeper/wider structure
- L4693 A minor variation of the Standard.

The contact angle of water on these substrates are displayed in Table 2.

Table 2: Contact angle of water on substrates

Substrate	Contact angle (°)
Stainless steel	84°
S Silicone	107°
S Standard	65°
S Nano	77°
S Fluoro	127°
K	89°
L4693	107°

Results and Discussion

Surface Deposition Results

The deposition tests in all cases gave a measurable weight gain due to the calcium carbonate crystals adhering to the surface. The brine was also precipitating in the bulk solution during the one hour and so during the test the supersaturation ratio

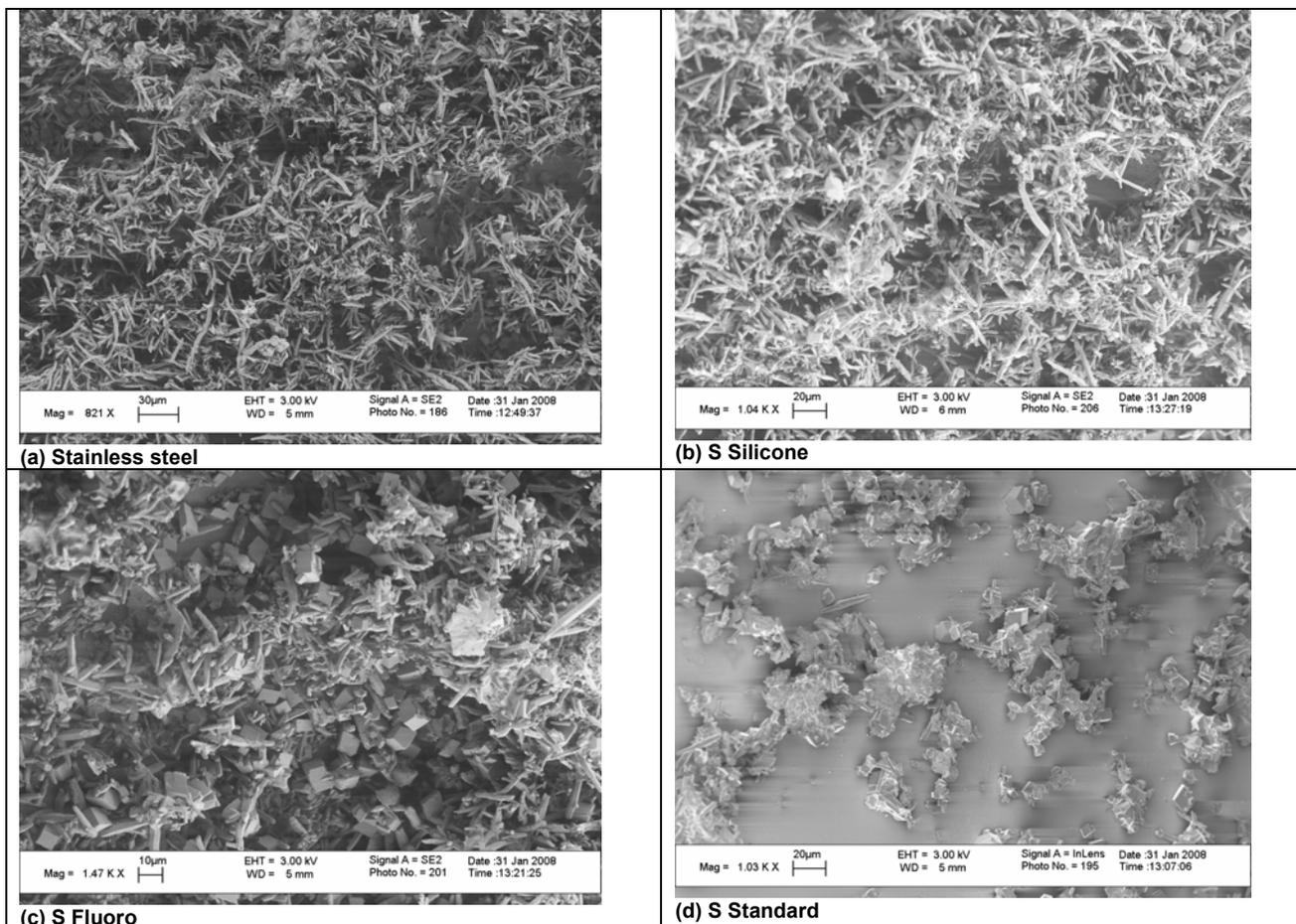
would be decreasing. For this study only the deposition at the end of one hour is measured and so there is no attempt to develop an understanding of the kinetics of the process. This step will come later as the work progresses. The induction time for the bulk precipitation was very short (less than 1 minute).

Table 3 gives the results of the deposition tests for the polymers and for the reference stainless steel sample. It is clear that most polymer surfaces (with the exception of S Fluoro and L4693) provide a significant reduction in the amount of scale on the surface but as interestingly there is a large range of performance amongst the polymer surfaces. The complete explanation for this is not presented in this paper but some initial correlations with macroscopic roughness and with contact angle are presented. Also, the microscopic images of the scale deposited on the surface are presented to assess the scale size versus the dimensions of the surface structures.

Table 3: Results of deposition tests

Surface	Average Mass Gain (mg)
Stainless steel	11.3
S Silicone	8.7
S Standard	3.75
S Nano	2.8
S Fluoro	11
K	8
L4693	11

Figures 4 a-g show the scale formation on the surfaces after the one hour test and it is clear that the stainless steel sample is entirely covered with needle-like crystals.



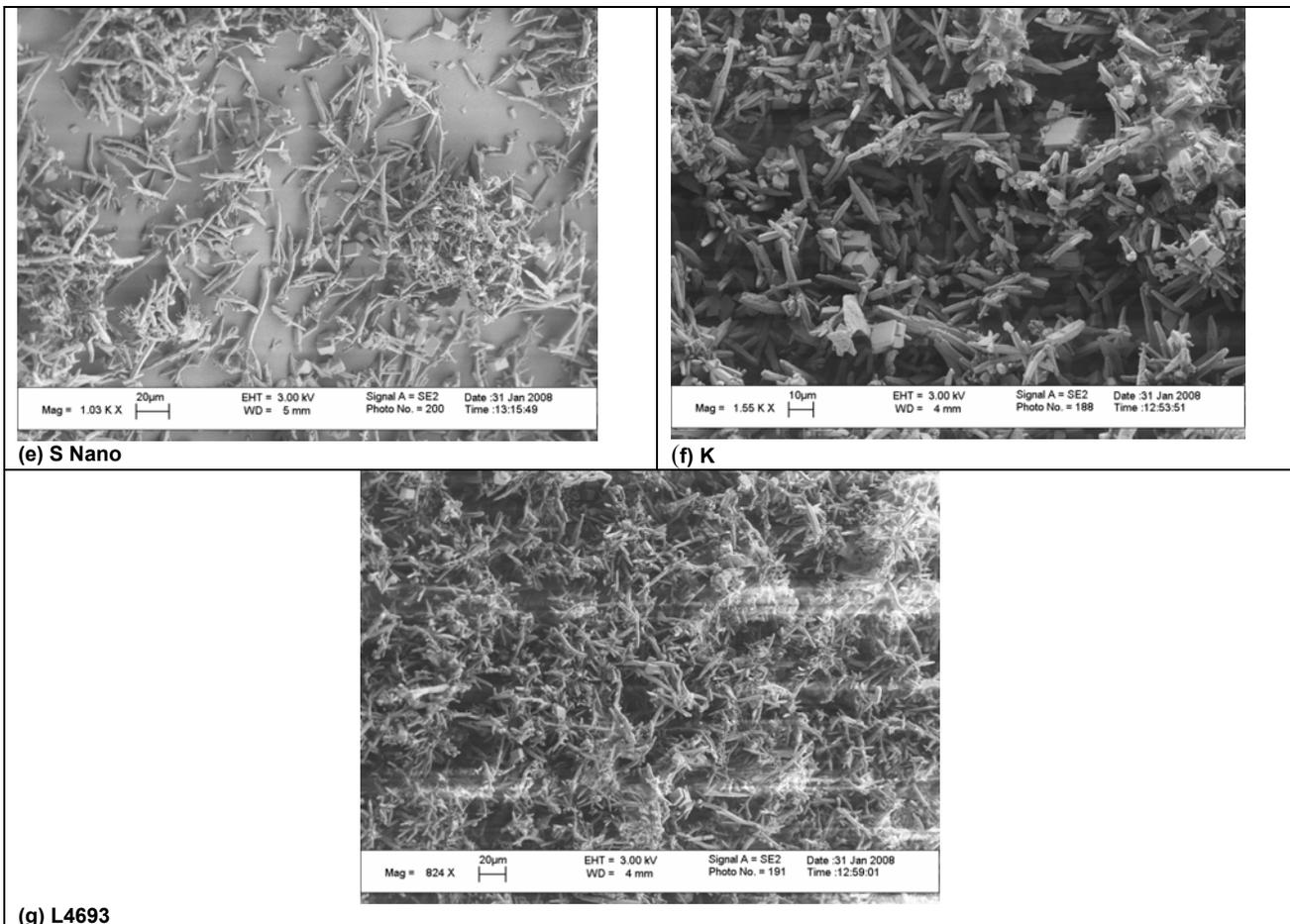


Figure 4: Scale deposition on sample surfaces after tests

Aragonite formation from this high supersaturated brine at 70°C is as expected. Some calcite crystals can be seen amongst the aragonite. Looking at the polymer surfaces it is also clear that for the S Silicone, S Fluoro, K and L4693, very little of the free surface of the polymer can be seen and this is an important point. The tendency of deposition and the kinetics of deposition of calcite onto calcite is what seems to be measured at the end of this test as any potential benefit offered from the polymer has been lost once it has become covered with scale. It is informative to know that it would seem that the benefits for some polymer surfaces are lost within such a short period of time but an important point is to understand what controls this initial deposition onto the polymer surface.

For the surfaces which are clearly still showing benefit there is still obvious free polymer surface visible and the images in Figure 5a-c show that the crystals, by the end of the hour test, are much larger than the structural features of the polymer surface. It is also interesting to note that the upper surface scale layer for all surfaces appears to be needle-like aragonite yet there is some evidence from the S Standard surface that the early scale formed is vaterite. It is not clear from the other surfaces whether there is vaterite as a bare layer of scale. Studying the early stages of deposition of scale-on-scale will enable these transformations to be studied in more detail.

Ideally to analyse the controlling factors for deposition it would be best to have a situation where crystals of CaCO_3 are only depositing onto the polymer but here there is clearly deposition onto CaCO_3 and the discussion will put the importance of this in context.

Figures 6 and 7 show a plot of contact angle versus deposition and also macroscopic roughness, R_a (measured by a Talysurf contact profiler) versus deposition. From these plots a few interesting features emerge which direct thinking in relation to the controlling factors in deposition. In looking at the points in region 1 in Figure 6 it is clear that the roughness of stainless steel is much higher than all of the polymer surfaces. Higher roughness has been associated with enhanced deposition in the literature and the reason for that is primarily due to the additional heterogeneous sites for nucleation at the protruding surface asperities. However, from this study it is clear that a difference of an order of magnitude in roughness (cf S Fluoro and stainless steel) offered very little difference in scaling. This is most likely attributed to the surface chemistry of the polymer which rendered it more susceptible to scaling. In a similar manner amongst the polymer samples, comparable roughnesses led

to more than a threefold difference in deposition. Whilst roughness appears to be an important factor it does not appear to be a dominating factor in agreement with the work reported in a previous paper (Zhi Wang, Anne Neville and A. W. Meredith 2005). Surface chemistry of the surfaces thus plays a major role in affecting adhesion too. From the water contact angle values, it can be seen that S Nano and S Standard have the lowest value amongst the rest, and can be deduced to have relatively higher surface energies than the other polymers.

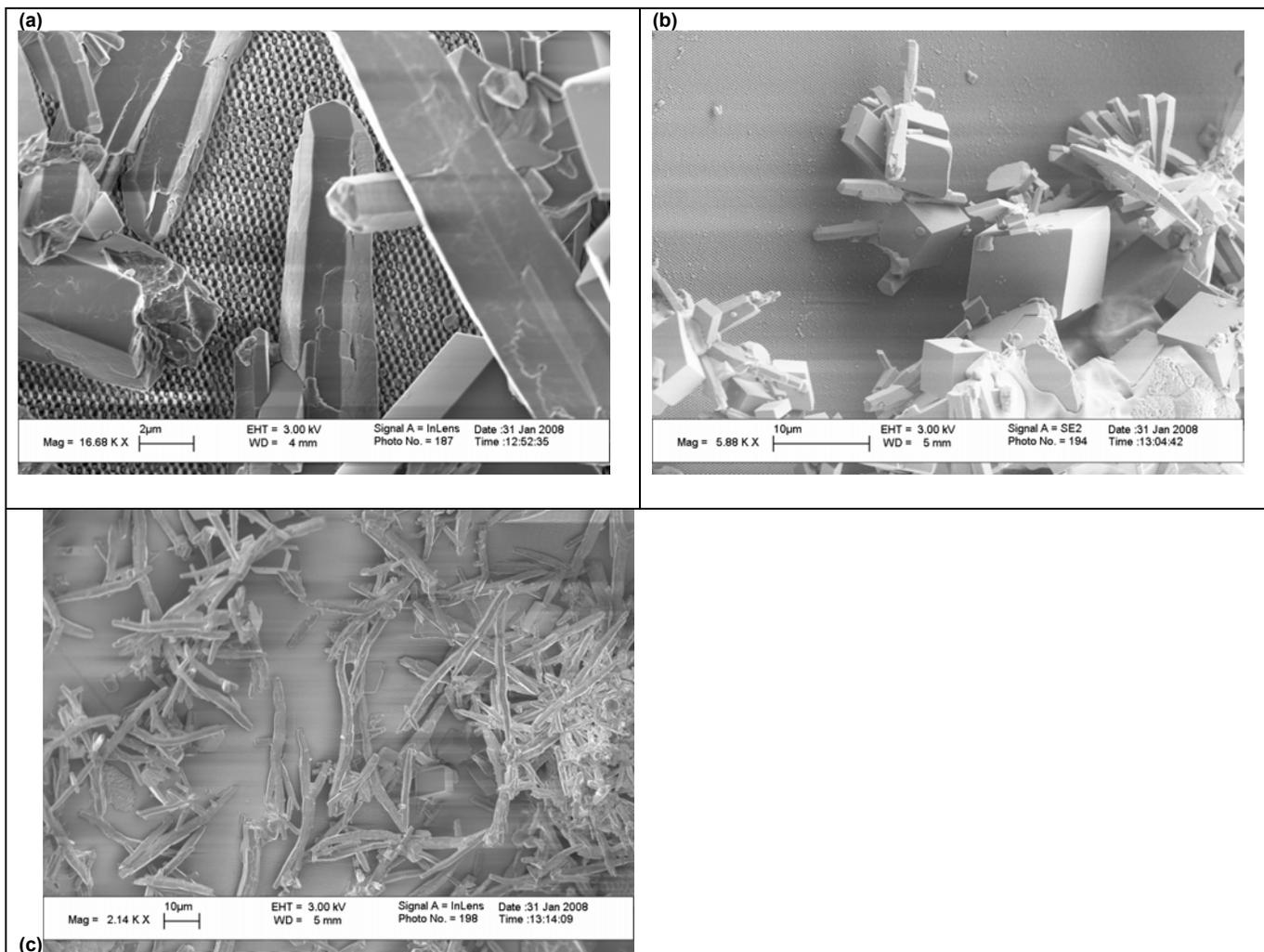


Figure 5: Crystal Deposition at higher magnification on S Standard and S Nano surfaces

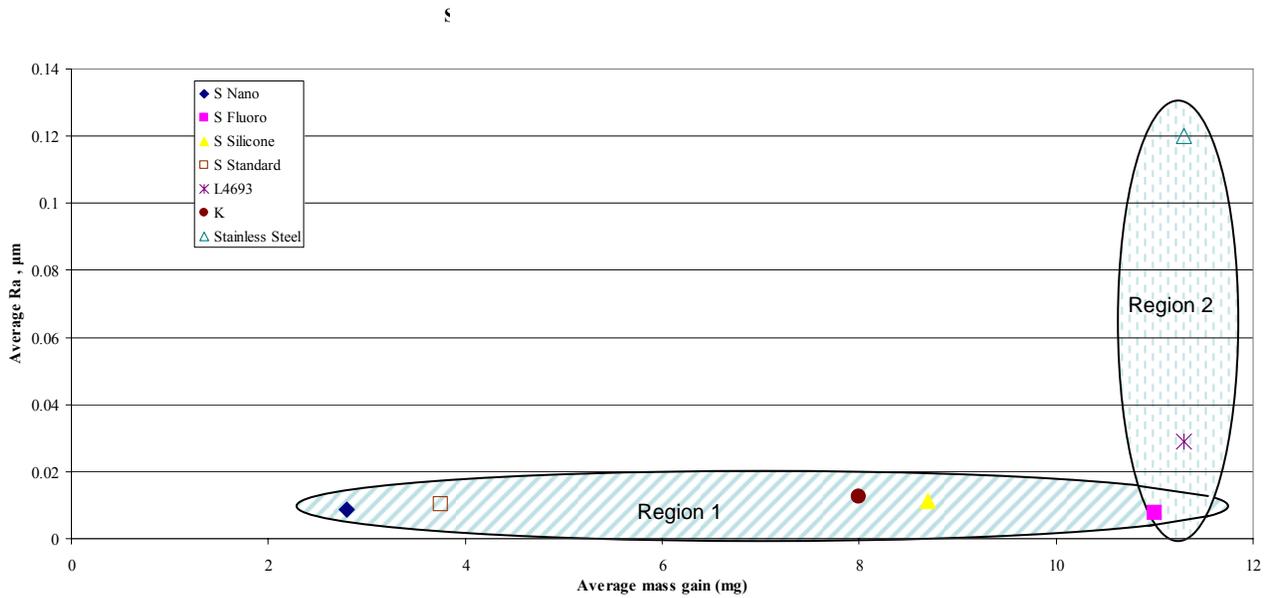


Figure 6: Graph of surface roughness (μm) versus scale deposition (mg)

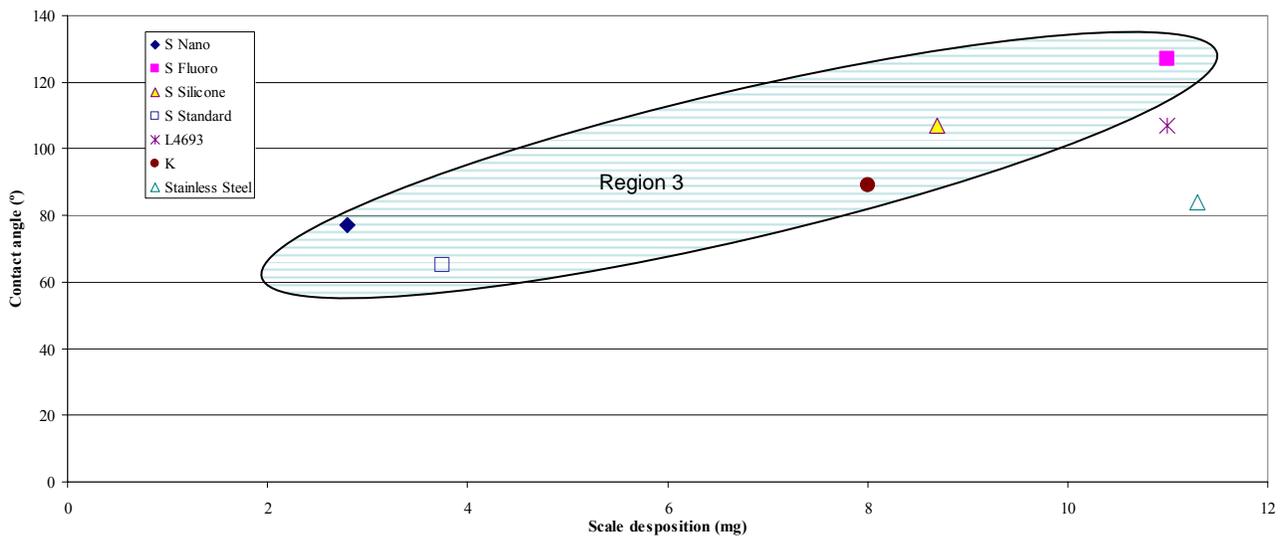


Figure 7: Graph of contact angle (°) versus scale deposition (mg)

In the literature associated with fouling, whether it be organic or inorganic, there is a general appreciation that the lower the surface energy the lower the propensity for scale formation. This was also found by the current author across a range of steel, diamond-like carbon and PTFE surfaces as a general loose correlation (Zhi Wang et al. 2005). This current work is illustrating that the situation is much more complex than this and a contact angle assessment cannot be used to predict scaling tendency. Amongst the surfaces with similar roughnesses (S Nano, S Standard, K, S Silicone and S Fluoro), as defined by region 3 in Figure 7, there is an opposite trend of higher scaling tendency for lower surface energy surfaces. Indeed it is clear that the two surfaces that offer the best scaling resistance (S Nano and S Standard) have the highest surface energy, a relatively low surface roughness and a nanostructure with inter-feature spacing of approximately 250nm. For the surface with the highest tendency for scaling L4693 it is interesting to note that the “mounds” are 3μm apart – this is probably enabling crystals to nucleate as the mounds act like nucleation sites. For the other structure the spacing is such that the deep grooves beside each column prevent asperities being seen as nucleation sites. The liquid will not wet the interior walls of the structure.

This work has shown that the parameters that affect surface scaling are complex and as such this preliminary study has opened up more questions than it has answered. However, it has pointed to the fact that although the polymers are offering benefit, the benefit is fairly short lived for some of the surfaces. To completely understand what must be done to design a surface which will give a long last effect the next step in this study must be to assess the controlling surface features for that first CaCO₃-on-polymer layer and not extend beyond this. Taking measurements when the surface has been completely covered gives some assessment of potential benefit but does not help in understanding the mechanisms by which these surfaces may be optimised. This is the direction for the future work in this area.

Conclusions

The surfaces mimicking the moth eye antireflective surface with a dual nanostructure have been shown to offer potential in terms of deposition resistance for mineral scale. The controlling features of the surfaces have been discussed and it is concluded that there are a complex combination of physical, chemical and topographical features which dictate the level of scaling. To fully understand how to design a surface for low fouling resistance it is necessary to focus on the initiation stage of scaling – where CaCO₃ forms on polymer and conduct tests in this regime. Going beyond this means that the scale forms on scale and any potential effect of the substrate is lost.

Acknowledgements

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References

Abdel-Aal, N. and Sawada, K. 2003. Inhibition of Adhesion and Precipitation of CaCO₃ by Aminopolyphosphonate. *Journal of Crystal Growth* **256**: 188-200.

Bornhorst, Antje, Muller-Steinhagen, H. and Zhao, Qi 1999. Reduction of Scale Formation Under Pool Boiling Conditions by Ion Implantation and Magnetron Sputtering on Heat Transfer Surfaces. *Heat Transfer Engineering* **20**(2): 6-14.

Briscoe, B. J. and Panesar, S. S. 1992. Effect of surface topography on the adhesion of poly(urethane) - metal contacts. *Journal of Physics D: Applied Physics* **25**(1A): A20-A27.

Carlos, A. Barrios, Qingwei, Xu, Teresa, Cutright et al. 2004. Incorporating zosteric acid into silicone coatings to achieve its slow release while reducing fresh water bacterial attachment. *Colloids and Surfaces* **41**: 83-93.

Cheng Y T, Rodak D E, Wong C A et al. 2006. Effects of micro- and nano-structures on the self-cleaning behaviour of lotus leaves. *Nanotechnology* **17**(2006): 1359-1362.

Dalas, Evangelos and Koutsoukos, Petros G. 1990. Calcium Carbonate Scale Formation and Prevention in a Flow-Through System at Various Temperatures. *Desalination* **78**: 403-416.

Forster, M. and Augustin, W. 1999. Influence of the adhesion force crystal/heat exchanger surface on fouling mitigation. *Journal of Chemical Engineering and Processing* **38**: 449-461.

Frederic, Bretagnol, Michael, Lejeune, Andri, Papadopoulou-Bouraoui et al. 2005. Fouling and non-fouling surfaces produced by plasma polymerization of ethylene oxide monomer. *ActaBIOMATERIALIA* **2**: 165-172.

Gill, Jasber S. 1999. A Novel Inhibitor for Scale Control in Water Desalination. *Desalination* **124**: 43-50.

Hadley, J. S. and Harland, L. E. 1987. Electroless Nickel/PTFE Composite Coatings. *Metal Finishing* **85**: 51-53.

Hanein, Y., Vickie Pan, Y., Ratner, B. D. et al. 2001. Micromachining of non-fouling coatings for bio-MEMs applications. *Sensors and Actuators B* **81**: 49-54.

Jeffrey, L. Dalsin and Phillip, B. Messersmith 2005. Bioinspired antifouling polymers. *Materials Today* **September**: 38-46.

Katainen, J., Paajanen, M., Ahtola, E. et al. 2006. Adhesion as an interplay between particle size and surface roughness. *Journal of Colloid and Interface Sciences* **304**: 524-529.

Krupp, H. 1967. Particle adhesion theory and experiment. *Advances in Colloid and Interface Science* **1**(2): 111-239.

- Lee, Seung-Mo, Lee, Hyun Sup, Kim, Dong Sung et al. 2006. Fabrication Of Hydrophobic Films Replicated From Plant Leaves In Nature. *Surface & Coatings Technology* **201**: 553-559.
- Miriam, Perez, Guillermo, Blustein, Monica, Garcia et al. 2005. Cupric tannate: A low copper content antifouling pigment. *Progress in Organic Coatings* **55**: 311-315.
- Muller-Steinhagen, H. and Zhao, Q. 1997. Investigation of low fouling surface alloys made by ion implantation technology. *Chemical Engineering Science* **52**(19): 3321-3332.
- N. Filip, Granit, E., Korin and A., Bettelheim 2003. Effect of Organic Additives on Electrochemical Surface Precipitation and Polymorphism of CaCO₃. *Chemical Engineering Technology* **26**(3): 341-346.
- Nishira, M. and Takano, O. 1994. Friction and Wear Characteristics of Electroless Ni-P-PTFE composite coatings. *Plating and Surface Finishing* **81**: 48-50.
- Ochoa, N.A., Masuelli, M. and Marchese, J. 2005. Development of charged ion exchange resin-polymer ultrafiltration membranes to reduce organic fouling. *Journal of Membrane Science* **278**: 457-463.
- Oliveira, R. 1997. Understanding Adhesion: A Means for Preventing Fouling. *Experimental Thermal and Fluid Science* **14**: 316-322.
- Parlaktuna, Mahmut and Okandan, Ender 1989. The Use of Chemical Inhibitors for Prevention of Calcium Carbonate Scaling. *Geothermics* **18**: 241-248.
- Rankin, R. H. and Adamson, W. L. 1973. Scale formation as related to evaporator surface conditions. *Desalination* **13**: 63.
- Roques, H. and Girou, A. 1974. Kinetics of the formation conditions of carbonate tartars. *Water Research* **8**(11): 907-920.
- Tabor, D. 1977. Surface forces and surface interactions. *Journal of Colloid and Interface Sciences* **58**(1): 2-13.
- Wang, Zhi, Neville, Anne and Meredith, A. W., 2005. How and why does scale stick - Can the surface be engineered to decrease scale formation and adhesion? SPE Seventh International Symposium on Oilfield Scale 2005: Pushing the Boundaries of Scale Control, Proceedings. SPE Seventh International Symposium on Oilfield Scale 2005: Pushing the Boundaries of Scale Control, Proceedings. Society of Petroleum Engineers, Richardson, TX 75083-3836, United States, Aberdeen, United Kingdom, pp. 85-92.
- Yang, Q. F., Ding, J. and Shen, Z. Q. 2000. Investigation on Fouling Behaviors of Low-Energy Surface and Fouling Fractal Characteristics. *Chemical Engineering Science* **55**: 797-805.
- Yang, Q. F., Ding, J. and Shen, Z. Q. 2000b. Investigation of Calcium Carbonate Scaling on ELP surface. *Journal of Chemical Engineering of Japan* **33**: 591-596.
- Yang, Q. F., Liu, Y., Gu, Anzhong et al. 2002. Investigation of Induction Period and Morphology of CaCO₃ Fouling on Heated Surface. *Chemical Engineering Science* **57**: 921-931.
- Yang, Q. F., Xu, D. Q. and Shen, Z. Q. 1994. A Theoretical Analysis and Experimental Study of the Induction Period of Calcium Carbonate Scaling. *Journal of Chemical Industry and Engineering (China)* **45**: 199-205.
- Zhao, Q. and Liu, Y. 2004. Investigation of Graded Ni-Cu-PTFE Composite Coatings with Antiscalting Properties. *Applied Surface Science* **229**: 56-62.
- Zhao, Q., Liu, Y., Wang, C. et al. 2005. Effect of surface free energy on the adhesion of biofouling and crystalline fouling. *Chemical Engineering Science* **60**: 4858-4865.
- Zhao, Q. and Wang, X. 2004. Heat transfer surfaces coated with fluorinated diamond-like carbon films to minimize scale formation. *Surface & Coatings Technology* **192**: 77-80.