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Liquid Infused Porous Surfaces for Mineral Fouling Mitigation

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ABSTRACT Preventing mineral fouling, known as scale, is a long-standing problem for a broad range of industrial applications ranging from oil production to water treatment systems to names but a few. The build-up of inorganic scale such as calcium carbonate on surfaces and facilities is undesirable as it can result in safety risks and associated flow assurance issues. To date the overwhelming amount of research has mainly focused on chemical inhibition of scale bulk precipitation and little attention has been paid to deposition onto surfaces. The development of novel more environmentally-friendly strategies to control mineral fouling will most probably necessitate a multifunctional approach including surface engineering. In this study, we demonstrate that liquid infused porous surfaces provide an appealing strategy for surface modification to reduce mineral scale deposition. Microporous polypyrrole (PPy) coatings were fabricated onto stainless steel substrates by electrodeposition in potentiostatic mode. Subsequent infusion of low surface energy lubricants (fluorinated oil Fluorinert FC-70 and ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIm)) into the porous coatings results in liquid-repellent slippery surfaces.

To assess their ability to reduce surface scaling the coatings were subjected to a calcium carbonate scaling environment and the scale on the surface was quantified using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). PPy surfaces infused with BMIm (and Fluorinert to a lesser extent) exhibit remarkable antifouling properties with the calcium carbonate deposition reduced by 18 times in comparison to untreated stainless steel. These scaling tests suggest a correlation between the stability of the liquid infused surfaces in artificial brines and fouling reduction efficiency. The current work shows the great potential of such novel coatings for the management of mineral scale fouling.

INTRODUCTION Preventing mineral scale build-up (such as calcium carbonate and barium sulphate) is an important challenge in many industrial installations such as desalination plant, heat transfer equipment or oil production facilities [1-6]. Mineral scale fouling costs money by reducing the efficiency of systems, and can in the worst case scenario result in safety hazards [7]. There are many approaches currently available to remove and prevent scaling with kinetic scale inhibitors, chemical scale dissolvers and mechanical methods being the most prevalent ones [8, 9]. Each of these techniques has its own advantages depending on the type of deposit and its location. However, these costly techniques can have a detrimental impact on the environment and desirable performance efficiencies are sometimes not achievable. Therefore it is believed that there is a potential cost benefit for alternative methods that could prevent mineral-fouling more effectively or be a supplement to the existing strategies. An alternative way forward identified is to turn to surface engineering - this is a very successful approach in the control of bio-fouling[10, 11] but only a few attempts have been made to use it for the purpose of mineral scale prevention due to the various physico-chemical mechanisms occurring often simultaneously (*e.g.* particle adhesion, heterogeneous crystal nucleation and growth) [12, 13]. In that regard it is highly unlikely that surface engineering designs based on one attribute only (e.g., surface topography) will successfully prevent scale build-up, and effective new coating technologies will most likely need to be multifunctional (i.e., incorporate a range of surface and bulk properties such as surface energy, topography, elasticity or softness). Rough textured surfaces with liquid repellent properties have shown promising performance for the control of surface fouling [12]. Originally inspired by nature [14, 15], such designs impart super-hydrophobicity by trapping air pockets within the texture [14-16]. However maintaining the stability of such systems can be a challenge because of the fragility of the air pockets that can collapse under the influence of external factors (*e.g.* hydrodynamic shear forces, external wetting pressures, diffusion through the liquid phase) [17, 18]. A novel approach to enable stable nonwetting properties involves replacing the delicate air pockets by an ad-hoc lubricant that preferentially wets the substrate. The microporous structure of the substrate is also of paramount importance as it contributes to securing the lubricant by capillary forces. This in turn confers stability to the resulting liquid infused porous surface. Inspired by the leaves of the pitcher plant, this novel class of liquid impregnated surfaces exhibits remarkable properties such as liquid repellency, smoothness or self-healing (by capillary motion upon damage) [19-21]. In addition recent studies have shown that such surfaces can demonstrate promising anti-biofouling as well as anti-icing properties [10, 22, 23]. The current study reports primarily on evaluating antifouling performances of liquid infused porous surfaces in a calcium carbonate ($CaCO_3$) scaling environment. The effect of two different lubricants is also explored.

EXPERIMENTAL SECTION

Surface Preparation. All reagents employed were of American Chemical Society (ACS) grade or finer and were used without further purification unless otherwise stated. The fabrication of a microporous overcoating by electro-polymerization of polypyrrole (PPy) was carried out using a conventional method [24-26]. Stainless steel discs (UNS S31603) (25mm diameter) were used as the working electrode in a standard potentiostatic three-electrode cell system (galvanostat Model 263A controlled via corrware software). A platinum wire was used as a counter electrode and a silver/silver chloride (Ag/AgCl) electrode was used as reference electrode. An electrolyte solution containing 0.1M pyrrole and 0.1 M $NaNO_3$ was used for the potentiostatic deposition of PPy. It was previously reported that the microstructure of PPy can be modified by varying the counter ion size [27]. In the present study, small sized nitrate anions (1.89 Å) were used to enhance their incorporation into the film thus improving the polymer oxidation process. A constant voltage of 0.85 $V_{/Ag/AgCl}$ was applied for 600 seconds during which the stainless steel surface was gradually coated by a PPy film exhibiting a final thickness of 4-5 µm.

The samples were then washed with ultrapure water and dried with nitrogen. Prior to applying the lubricants, the samples' hydrophobicity were enhanced by depositing a fluorocarbon film using a reactive ion etching apparatus and trifluoromethane (CHF_3) as precursor gas. An excess of fluorinated lubricant (Fluorinert FC-70) or ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIm) were applied into the hydrophobic PPy surfaces; both lubricants have already been used successfully elsewhere for the preparation of liquid infused surfaces [19, 20].After a 12 hours period to allow the lubricants to fully infuse the microporous PPy; the samples were tilted and a stream of nitrogen was used to assist removal of the excess lubricant.

Surface Characterization. *Scanning Electron Microscopy (SEM).* Porous PPy coatings were examined using a Carl Zeiss EVO MA15 SEM. The samples were sputtered with a 30 nm thick gold layer before observations and an accelerating voltage of 2 kV was used for the measurements.

Surface Wettability. Surface wettability of liquid infused porous surfaces was evaluated by contact angle goniometer measurements. The so-called (static) advancing and receding water contact angle values presented in Figure 2 are the mean from at least 10 measurements in different locations; errors bars represent the standards deviation.

Scaling Tests. *Scale Surface Growth.* Anti-scaling properties of the surfaces were assessed in a calcium carbonate scaling environment. The liquid infused porous surfaces have been tested using a standard bulk jar test where precipitation occurred in static conditions at atmospheric pressure and low temperature (50°C). Two simple brines (one containing the cations and the other containing the anions of the scale of interest) were prepared by weighing the appropriate quantity of salts and mixing with ultra-pure water ($\rho \approx 18$ MΩ·cm). Their compositions (reported in Table 1) are not based on any specific field and were designed for the sole purpose of giving severe scaling conditions. Mineral scale was precipitated spontaneously by mixing 500 ml of each brine preheated to 50°C. Before mixing, the carbonate brine was buffered to pH of 6.8 by bubbling CO_2 gas at 6000cm^3/hour. CO_2 bubbling was maintained throughout the experiment. The saturation index was calculated with Multiscale software and found to be SI≈2.6. After 2 hours immersion, the sample was rinsed with distilled water and dried in an oven for an hour at 120℃. In order to obtain the scaling tendency of the surfaces, calcium carbonate was dissolved (in EDTA solution $1.7 \cdot 10^{-2}$ M, pH 11) and analyzed by ICP-AES. These tests were carried out using three replicates. This test assesses the ability of the surface to reduce nucleation and growth of scale at the surface by a heterogeneous nucleation process.

Table 1 Brine composition and saturation index for calcium carbonate scaling experiments

Salt	Brine 1 (g.l^{-1})	Brine 2 (g.l^{-1})
NaCl	10.625	10.625
$CaCl_2.6H_2O$	31.486	-
$NaHCO_3$	-	12.102
Saturation index	2.6	
Precipitation	3.4 g.l^{-1}	

Scale Surface Adhesion. Adhesion tests were performed by immersing the liquid infused surfaces in the scaling brine once precipitation in the bulk solution had occurred and reached a steady state. At this point the solution was turbid and there was a high degree of solids particles precipitated in the solution. The surfaces were immersed 24 hours after the scaling brines were mixed at which time calcium carbonate crystals would have fully precipitated in the bulk solution. After 2 hours immersions, the samples were rinsed with distilled water and the amount of calcium carbonate was analyzed by ICP-AES. This test assesses the ability of the surface to reduce adhesion of pre-formed particles.

RESULTS AND DISCUSSION

Surface Characterization. SEM images of the PPy overcoating in **Figure 1** exhibit a rough and globular structure with size ranging from sub micrometre up to several microns. Higher magnification images reveal the hierarchical nature of the PPy film where individual spheroids are formed of smaller nanoscale features enhancing the surface area of the film as well as the retention of the lubricant. The specific area measurement shows a large BET surface area of 13.3 ± 0.7 $m^2.g^{-1}$ (see associated content).

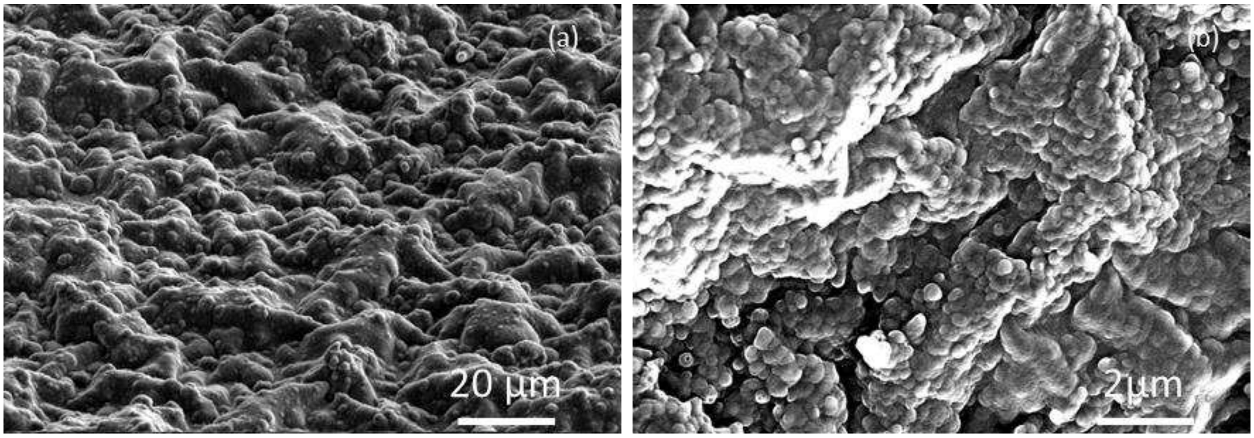

Figure 1(a-b) Scanning electron micrographs of microporous PPy film at magnification X500 and X5000 respectively.

The stability of liquid infused porous surfaces in seawater and especially their ability to preserve their hydrophobicity is of paramount importance if they are serious contenders for use in technical applications. To assess their performance in such an environment, surface wettability of fresh prepared liquid infused surfaces was also monitored after 12 and 24 hours immersion in synthetic sea water (3 wt% NaCl). Freshly PPy surfaces infused with Fluorinert FC-70 exhibit an advancing water contact angle of 102º as well as a low hysteresis (3º). However after a 24 hours immersions in synthetic sea water, the water contact angle hysteresis increases dramatically to 52º. This was attributed to the ability of the lubricant to spread and cloak over water, leading to the gradual loss of infused oil through entrainment in the water flow occurring in the vicinity of the surface. As the lubricant is depleted, the roughness of the surface is once more accessible which leads to the increase of contact angle hysteresis observed. Water contact angle measured on BMIm infused surface is lower (71º) than measured on Fluorinert FC-70 due to the more moderate surface energy of the ionic liquid (18 and 34 mN/m for Fluorinert FC-70 and BMIm respectively [28]). After immersion for 24 hours in synthetic sea water, the measured advanced and receding contact angles remained unchanged. The stability of BMIm infused surfaces was attributed to the negative spreading coefficient of BMIm over water (i.e. the ionic liquid does not cloak over water) as well as its non-miscibility in water [20].

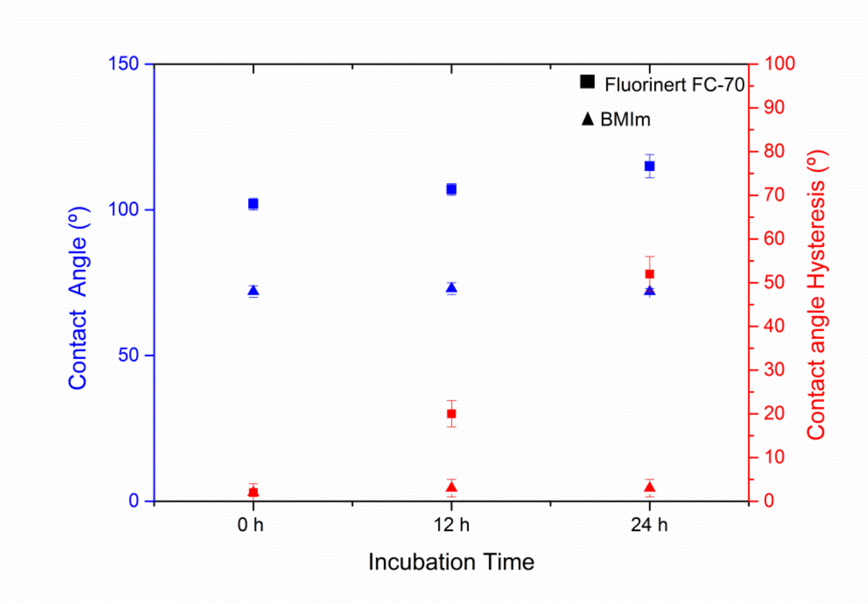

Figure 2 Water contact angle on Fluorinert FC-70 and BMIm infused porous surfaces.

Scaling Tests. *Scale Growth.* To assess the mineral anti-fouling properties of the liquid infused porous surfaces, scaling tests were carried out for 2 hours. Figure 4 shows the calcium carbonate mass gain on the different surfaces.

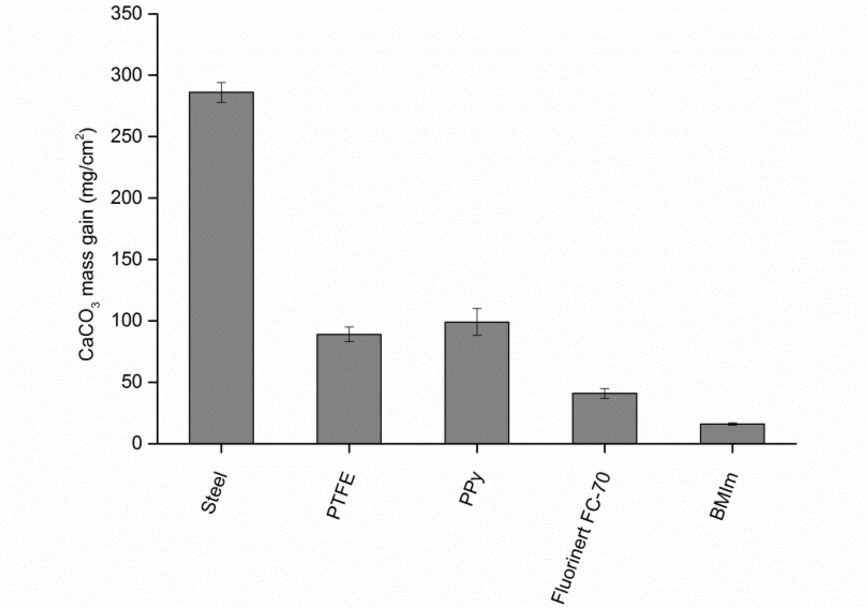

Figure 3 Mass gain per unit area of scale after 2h immersion in calcium carbonate ($CaCO_3$) scaling brine; error bars represent standard errors.

The highest deposition of calcium carbonate was measured on stainless steel 316L (286 mg·cm^{-2}); nearly 3 times the mass gain measured on uncoated PPy (99 mg·cm^{-2}). In addition, the BMIm infused porous surface showed the lowest amount of mineral scale (16 mg·cm^{-2}). However Fluorinert FC-70 infused surface shows slightly higher deposition of calcium carbonate (41 mg·cm^{-2}), a level comparable to that of PTFE (89 mg·cm^{-2}). Such results were explained by the partial loss of lubricant in the aqueous phase as suggested by the increase of water contact angle hysteresis. Surface topography is at least equally as important as surface energy for effective scaling control and the use of conventional (super-) hydrophobic surfaces have been reported to enhance scale build up under some conditions[12]. Indeed the presence of a micro or nanometre scale texture associated with such surfaces has often a detrimental effect by offering a multitude of nucleation sites for scale thereby facilitating its nucleation and growth on the surface. Such observations are in accordance with the high density of calcium carbonate observed on non-infused PPy and PTFE to a lower extent in the current work. Infusing the micro-porous PPy with lubricants lower the surface energy of the interface which increase the barrier energy for heterogeneous nucleation [29-32] and also help reducing the adhesion of solid particles onto the surface [33, 34] while maintaining a smooth surface; deflect free down to the molecular scale [19]. It is this multifunctional design that provides the liquid-infused porous surfaces with the promising antifouling properties shown in Figure 4. The SEM micrographs confirm the mass gain results presented in Figure 4; both liquid infused surfaces show only a limited number of crystals while stainless steel 316L exhibits a large amount of scale and clusters of crystals that have significantly grown out from the surface. Liquid infused surfaces display fewer crystals (Figure 4d-e) than the surfaces with poor anti-scaling properties while their size remains in the same order of magnitude. This suggests that the liquid infused surfaces act primarily to reduce the number of nucleation sites rather than inhibiting surface nucleation (which would lead to smaller crystals rather than a smaller population).

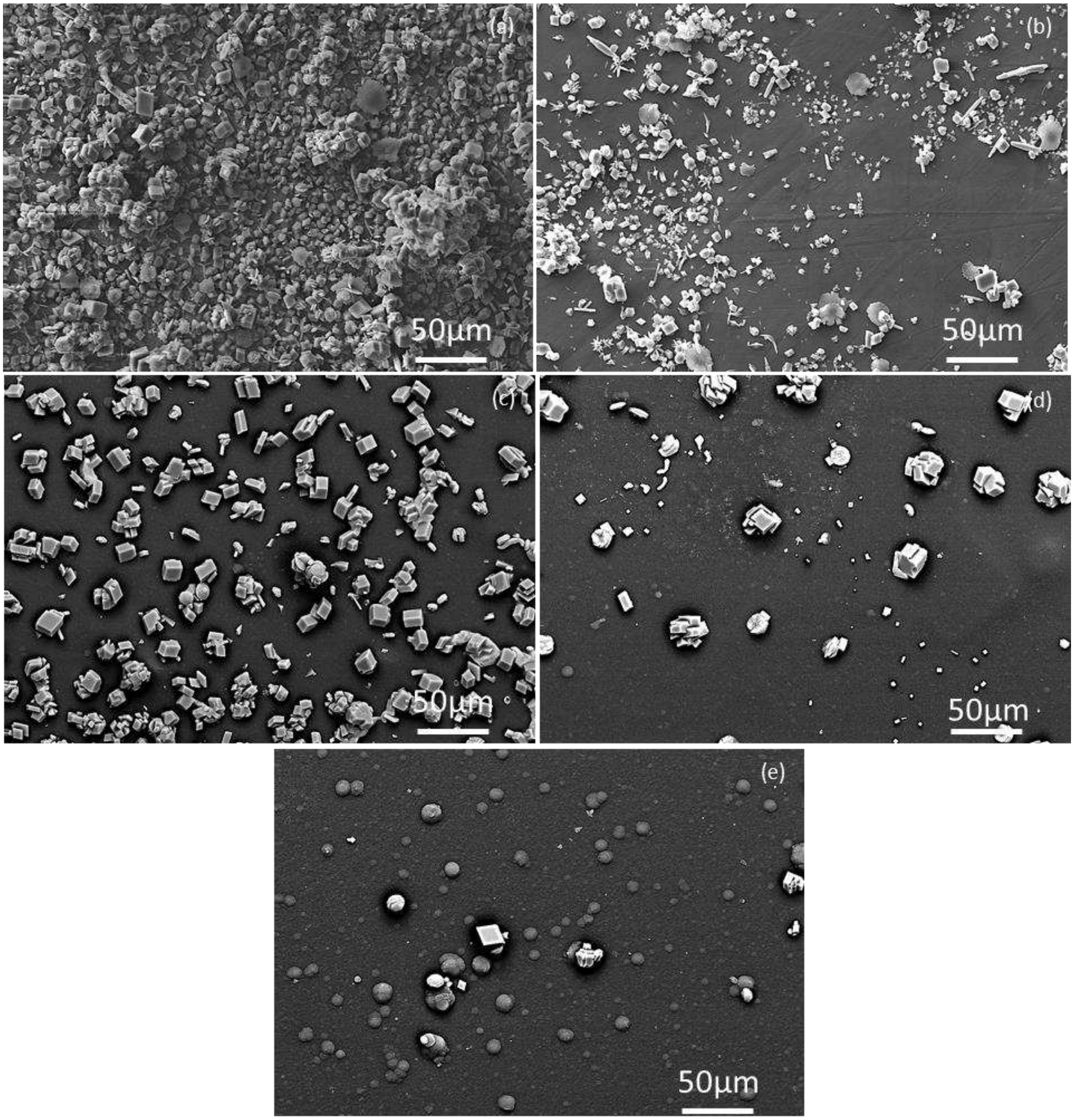

Figure 4 SEM micrograph of calcium carbonate crystals on (a): stainless steel 316l; (b):PTFE; (c): PPy overcoating; (d): Fluorinert FC-70 infused PPy; (e): BMIm infused PPy

Scale Surface Adhesion. Adhesion tests were performed by immersing the liquid infused surfaces in the scaling brine once precipitation in the bulk solution had occurred and reached a steady state; slow magnetic agitation ensured scale particles were kept in suspension. $CaCO_3$

mass gains values measured after 2 hours immersion are presented in Figure 5. Mineral scales appear to be much reduced compared to the scale deposition tests. The highest calcium carbonate mass was measured on stainless steel (41 mg·cm^{-2}), more than 10 times the mass gain measured on liquid infused surfaces (3 mg·cm^{-2}). PTFE and non-infused PPy exhibit a similar mass gain at 19 and 29 mg·cm^{-2} respectively. The relatively large error bars observed were attributed to the variation of crystal sizes that come into contact and adhere to the surfaces.

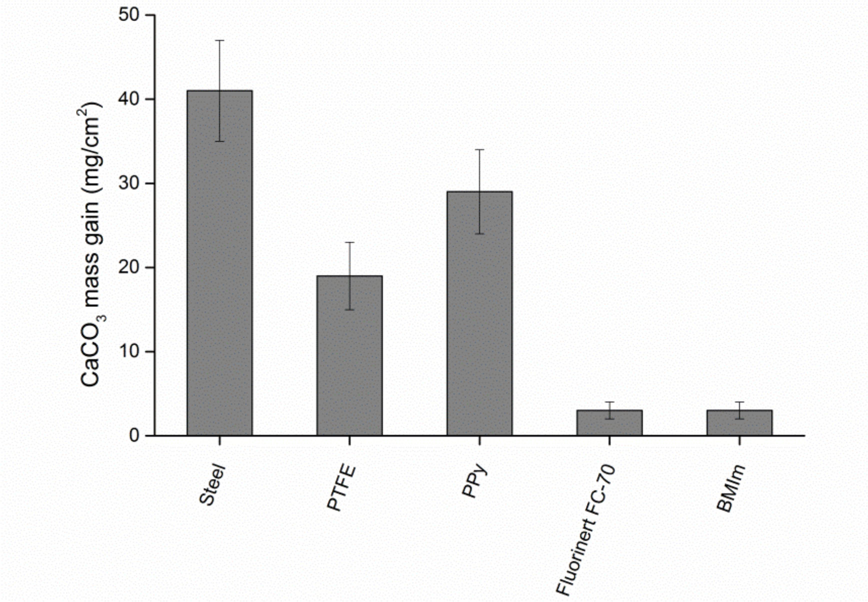

Figure 5 Density of scale after 2h immersion in pre-precipitated calcium carbonate (CaCO3) scaling brine; error bars represent standard errors.

These results shows that in the present study, the main process of surface fouling is likely to be the direct growth of crystals on the surface and the indirect adhesion or particulate deposition from the bulk solution is much less important. Hence, once bulk precipitation is complete, very little scale from the bulk solution actually adheres to the surface. However, the slippery and low adhesion properties of the liquid-infused surfaces and show an effect in reducing even further the adhesion of mineral scale.

CONCLUSIONS The current work investigates the potential of using surface engineering to mitigate mineral surface fouling. Based on the work published by Aizenberg *et al.* [19] liquid-infused porous surfaces were fabricated by electropolymerization of polypyrrole on stainless steel 316L substrates that were subsequently infused with Fluorinert FC-70 and BMIm. The resulting surfaces exhibited hydrophobic properties, low water contact angle hysteresis and BMIm infused surfaces also showed good stability when immersed in sea water. The liquid infused surfaces displayed good mineral antifouling properties by significantly reducing the build-up of calcium carbonate. Surface scaling is a complex phenomenon resulting from the combined effect of adhesions forces and heterogeneous surface nucleation mechanisms; by providing a smoothness as well as low adhesion properties liquid infused porous surfaces reduce both mechanisms more effectively. Although the current study is showing promising results future work should consider surfaces evaluation in more realistic conditions such as flowing systems and high salinity scaling environments. Because the electropolymerization process is simple, fast, and scalable to large areas with complex geometry, such surfaces are promising for use in various applications including oil production plants where the produced oil could potentially be used as the infused lubricant.

ASSOCIATED CONTENT PPy electrodeposition curves, AFM micrograph, white light interferometry, FT Raman spectrum, BET specific surface area measurement, ICP - AES measurements of [Ca^{2+}] and turbidity plots. This material is available free of charge as associated content.

AUTHOR INFORMATION

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Author Contributions

⊥These authors contributed equally to this work.

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