

Iron Carbonate Based Slippery Liquid Infused Porous Surfaces (SLIPS) for Enhanced Mineral Fouling Resistance

Alexander Saul
Institute of Functional Surfaces
School of Mechanical Engineering
University of Leeds
Leeds, LS2 9JT
United Kingdom

Anne Neville
Institute of Functional Surfaces
School of Mechanical Engineering
University of Leeds
Leeds, LS2 9JT
United Kingdom

Salima Baraka-Lokmane
Department of Flow Assurance and Treatment
Total S.A.
Pau Cedex, 64018
France

Aurelie Le Beulze
Innovation & Strategy Direction – R&D Division
Prospective Labs – Nanotechnologies &
Sensors
Total S.A.
Pau Cedex, 64018
France

Thibaut Charpentier
School of Chemical and Process Engineering
University of Leeds
Leeds, LS2 9JT
United Kingdom

Suparit Tangparitkul
School of Chemical and Process Engineering
University of Leeds
Leeds, LS2 9JT
United Kingdom

John-Richard Ordonez-Varela
Innovation & Strategy Direction – R&D Division
Prospective Labs – Nanotechnologies &
Sensors
Total S.A.
Pau Cedex, 64018
France

ABSTRACT

Inorganic surface fouling is a problematic issue that poses both economic and safety risks to a number of industries, particularly the oil and gas sector. Current scale prevention methods vary and can be both costly and inefficient. LIS (Liquid infused/Lubricant Impregnated Surfaces) or SLIPS (Slippery Liquid Infused Porous Surfaces) represent a new development that has the potential to provide a surface engineering solution to the scale dilemma. SLIPS are driven by a low surface energy lubricant held in place by a textured surface, underpinning the surfaces self-healing, self-cleaning and omniphobic

capabilities. In the current study, an original SLIPS has been fabricated on carbon steel by utilizing an iron carbonate corrosion by-product (FeCO_3) layer, functionalized with an aminosilane and infused with either fluorinated ionic liquid or fluorinated oil.

A combination of scanning electron microscopy and energy dispersive x-ray has been used to study the anti-fouling performance of the new surface in a high scaling CaCO_3 environment. Scaling tests indicate substantial reduction in scale on the FeCO_3 SLIPS compared to untreated carbon steel, the prevalent material used in oil and gas pipelines. Surface deposition and crystal adhesion mechanisms are disrupted with the SLIPS surface by reducing the density of nucleation sites and increasing the activation barrier to nucleation. These results shed light on the growing importance of surface engineering as an effective tool in the comprehensive management of scale. It also importantly exploits the naturally forming corrosion product (FeCO_3) and adopts it to give the surface scale reduction functionality. Normally the formation of FeCO_3 corrosion product complicates scale management.

Key words: Mineral scale, surface fouling, calcium carbonate, surface engineering, SLIPS

INTRODUCTION

Inorganic fouling remains a critical factor contributing to loss of production and safety issues in a variety of contemporary industrial processes.^{1,2} The scale problem is significant in the production of oil and gas where mineral deposits, particularly calcium carbonate (CaCO_3) and barium sulfate (BaSO_4) on the internal surfaces of pipelines/tubing, manifolds and safety valves lead to flow assurance concerns.^{3,4} Oilfield operators have a selection of proactive and reactive strategies for mitigating and removing scale, ranging from mechanical removal, scale inhibitors, dissolvers and SMART completions technology to name a few.^{5,6} Surface engineering or modification is another key prevention method that actively disrupts the mechanisms by which scale deposits and adheres to the surface interface.^{7,8}

Slippery Liquid Infused Porous Surfaces (SLIPS), otherwise known as Lubricant Impregnated/ Liquid Infused Surfaces (LIS) represent a growing technological development in the surface engineering world. The bio-inspired (*i.e.* Pitcher plant) concept, highlighted recently by Wong et al in 2011,⁹ comprises a textured/roughened substrate that has been infused with a lubricant, kept in place by the forces of surface energy and capillarity. The result is a surface operating under the Cassie-Baxter model,¹⁰ where the air pockets/gaseous phase (*i.e.* Lotus leaf) are replaced with a low surface energy fluid, removing potential drawbacks associated with compressibility and providing an omniphobic, self-healing and self-cleaning coating. The SLIPS surface has been tested successfully across a range of applications ranging from aerospace anti-icing to marine/medical anti biofouling.¹¹

The versatility of the SLIPS surface, coupled with additional qualities including resistance to extreme conditions (HP/HT) and drag reduction, make it an appealing surface solution for scaling problems in demanding environments.^{12,13} Previous research into the use of SLIPS for inorganic anti-fouling has focused on the application to a stainless steel substrate. Surface texture has been generated either by electro deposition of polypyrrole¹⁴ or polyaniline,¹⁵ or mechanical sand blasting¹⁶ and has shown promising results in scaling tests with general formation water, CaCO_3 dominated brine and Gypsum dominated brines. Whilst these surfaces have shown good antifouling behavior, the complexities and sensitivity of the surface texturing method are not easily transferrable to applicable industrial materials.

The focus of this research is the anti-scaling performance of an original and practical SLIPS combination in a CaCO_3 scaling environment. Because the ultimate application of scale control is for oil and gas handling pipelines, X65 carbon steel has been chosen as the base substrate. Surface texture has been created by incorporating the iron carbonate corrosion product from the aqueous CO_2 corrosion conditions commonly found in pipelines. FeCO_3 is a robust substrate with solid mechanical properties (*i.e.* tensile

strength, hardness etc.) and the ability to also reduce corrosion rates that make it a suitable SLIPS layer in a pipeline environment.¹⁷ The two lubricants tested were ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM) and Krytox vacuum oil VPF1525. A combination of surface characterization techniques has been used to further understanding the anti-scale mechanisms of SLIPS surfaces.

EXPERIMENTAL PROCEDURE

Material Preparation

Seven samples were tested, representing different conditions found in a pipeline (Figure 1). This included two SLIPS combinations (Krytox and BMIM), duplicate SLIPS combinations but with the application of a silane layer before lubrication, an initial iron carbonate base layer (i.e. corroded pipe) and an untreated plain X65 carbon steel sample (i.e. fresh pipe).

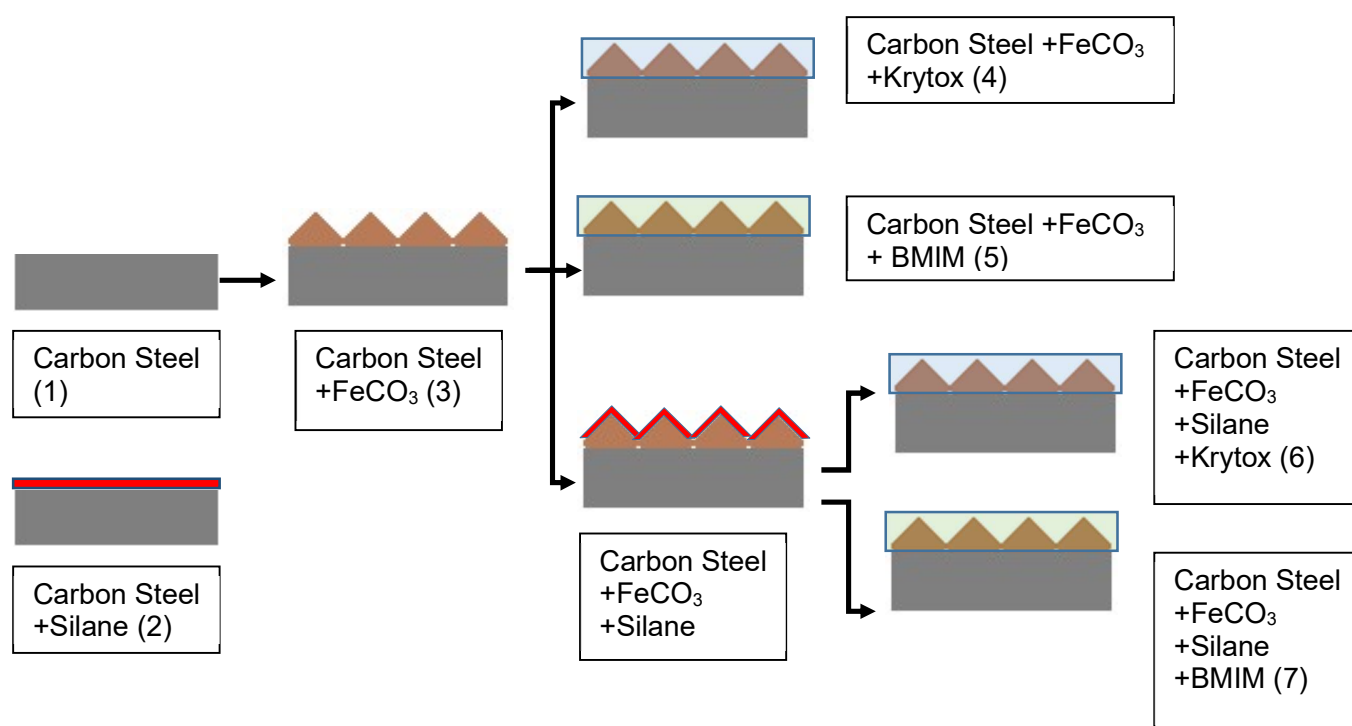


Figure 1: Schematic of SLIPS fabrication, numbers denote samples tested.

X65 Carbon Steel (CS) of elemental composition shown in Table 1 was machined into discs with diameter 25 mm and thickness of 6 mm. Samples are cast in a non-reactive resin, with one circular face exposed and a wire for suspension. Discs were wet polished successively with 120p, 320p, 600p silicon carbide paper (SiC) and rinsed with DI water. Final R_a (average arithmetic roughness) value on average $0.1\mu\text{m}$.

Table 1

Elemental Composition of X65 Carbon Steel Samples

C	Si	Mn	P	S	Cr	Mo	Ni
0.12%	0.18%	1.27%	0.008%	0.002%	0.11%	0.17%	0.07%
Cu	Sn	Al	B	Nb	Ti	V	Fe

0.12%	0.008%	0.022%	0.0005%	0.054%	0.001%	0.057%	97.8075%
-------	--------	--------	---------	--------	--------	--------	----------

Fabrication of iron carbonate (FeCO_3) layer

X65 carbon steel samples were exposed to aqueous CO_2 corrosion to produce an iron carbonate layer for the SLIPS system. CO_2 corrosion, much like scale is a prevalent production and safety issue that dominates the oil and gas industry. The fabrication method has been chosen given the natural tendency of carbon steel surfaces to corrode in-situ. The presence of iron carbonate (FeCO_3) layers has already been associated with reducing corrosion rates and has been chosen as a simple and environmentally-friendly method of fabricating surface topographical features for SLIPS. The growth conditions have been chosen based on prevailing literature for favorable production of FeCO_3 protective films.^{18,19,20}

Iron carbonate has been fabricated in a standard CO_2 corrosion bubble cell set up. Solution chemistry for the fabrication of the iron carbonate base layer consisted of 20g of NaHCO_3 (0.24M) and 3.5 wt % NaCl. The solution is then bubbled with CO_2 for 24 h prior to start, with on average a pH level above 7. A magnetic stirrer is operating at 150 rpm to ensure uniform solution consistency throughout the experiment. Temperature is maintained at 80°C with a test duration of 72 hours. Presence of FeCO_3 is confirmed by XRD and SEM.

Electrochemical Setup

Electrochemical measurements were conducted using a computer controlled potentiostat (Ametek Solartron) along with Corrware software. The three electrode cell consisted of a X65 Carbon steel working electrode (WE), Ag-AgCl reference electrode and a platinum counter electrode (CE). LPR measurements were performed by polarizing the sample ± 15 mV vs. the open circuit potential OCP at a scan rate of 0.25 mV/s (in accordance with ASTM-G102). Environmental conditions and duration are the same as outlined above in the fabrication of iron carbonate section.

SLIPS prediction model

The model from Preston *et al* [21] was used to predict the stability of the SLIPS surface. This model is largely governed by interfacial relations between the 3 phases (impinging droplet, lubricant and solid surface) and a geometric factor (roughness). The model inputs are obtained from various surface characterization techniques outlined in the experimental section. For SLIPS systems 5 criteria for stability exist as outlined in Figure 2:

- I. The lubricant does not cloak the impinging droplet.
- II. The impinging fluid forms discrete droplets on the lubricant.
- III. The impinging droplet does not draw the lubricant away from the surrounding substrate.
- IV. The impinging droplet does not displace the lubricant on the substrate.
- V. The impinging droplet and lubricant are immiscible.

Ideally, with regards to a successful SLIPS system, all criteria should be satisfied. However there is a degree of flexibility in the criteria for scaling applications, particularly with regards to Criteria (I) and (II). With criteria (I), cloaking of the droplet can lead to lubricant depletion as the droplet sheds taking a thin film of lubricant with it. The extent of cloaking however can be minimal and with a reservoir source of lubricant, the effects on scaling would be minor as the lubricant barrier is maintained. Criteria (II) is more relevant to condensation applications, where a discrete droplet is necessary, in the case of scaling the lubricant barrier is retained and thus failure in this criteria would not have an adverse impact on scale performance. Failure in criteria (III), (IV) and (V) would lead to a direct breakdown of the protective