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Surface Inorganic Scale Formation in Oil and Gas Industry: as Adhesion and Deposition Processes

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1. Abstract

Scale formation on surfaces can normally be divided into two distinct processes: a "deposition process" which refers to the process of heterogeneous nucleation and growth at the asperities of the surface and an "adhesion process" which refers to the sticking of pre-existing crystals, which have nucleated in the bulk solution, and which build up as a layer on the surface. It has been presented in this paper that the surface scale formation rate is more dominantly controlled by the "deposition process" rather than the "adhesion process"; however, the level of agitation could have inverse effects on one process to another. Only a small amount of research has been done to understand the differences of the kinetics of each of these processes. The presented work represents an experimental study of scaling tests to assess the effect of hydrodynamic conditions, using Rotating Cylinder Electrode (RCE), in a complex scaling environment, particularly supersaturated with barium/strontium sulphate and calcium carbonate, on the stainless steel substrate coated with a wide range of different industrial coatings.

In addition, the effect of the surface energy and surface roughness on both processes has been studied. The paper provides data that will assist in the understanding of the controlling parameters in scale formation in different conditions, and also describes what characteristics of the surface can make it a good anti-scale surface for inorganic scale; however, the results have showed that merely one parameter cannot assure a surface as a good antifouling surface.

Keywords: Inorganic scale, adhesion, deposition, hydrodynamic effects, Rotating Cylinder Electrode (RCE).

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2. Introduction

Scale formation is recognized as one of the major flow assurance problems affecting production in the oil and gas sector. The main problems of scale deposits in oil and gas industries are clogging the wellbore, reducing equipment lifetime, affecting the integrity of components such as subsurface control valve (SSCV), Electrical Submersible Pumps (ESPs) and hydraulic actuators. The economic implications arise from reduced fluid flow and hence lower oil production but also the huge maintenance costs of replacing production lines.

In the oil and gas industry, many oil wells suffer from flow reduction due to scale deposition within the downhole utilities, valve applications, and tubular components especially during the oil recovery operations.

Inorganic scale deposits (e.g. $CaCO_3$, $BaSO_4$ and $SrSO_4$) can be deposited all along the water paths in the pipeline applications. Oil industries normally encounter two types of scale formation (Vetter ; Moghadasi *et al.* 2003b; Moghadasi *et al.* 2003a; Bader 2006) as follows:

(a) Carbonate scales ($CaCO_3$ and $FeCO_3$) take place where there is a change in temperature and pressure which results in the release of carbon dioxide from aqueous form to gas form from the flowing fluid.
(b) Sulphate scales ($BaSO_4$, $SrSO_4$, $CaSO_4$ and $CaSO_4.H_2O$) come about where there is a mixture of two incompatible brines.

At the early stages of the oil extraction process, due to large differences in temperature and pressure the carbonate scales are the dominant type of scales to form, while in the latest stages of oil extraction the sulphate scales are the dominant types. The reason is that in the Enhanced Oil Recovery (EOR) process seawater, which is abundant and cheap, is pumped down to the reservoir to increase the oil production. Seawater is rich in sulphate ions and reacts with cations (such as Ba^{2+} and Sr^{2+}) in the reservoir and the formation of sulphate scale can result. Although in some cases to prevent sulphate scale problems, de-sulphated seawater is injected into an oilfield, it is not economically efficient (Jordan *et al.* 2001).

Applying surface coatings or changing the physical/chemical nature of a surface can be a potentially good strategy to reduce the formation of scale at surfaces. In developing a surface engineering strategy for scale, it is particularly important to understand the effect of some parameters in reducing scaling such as: surface parameters (e.g. the roughness (Keysar *et al.* 1994; Cheong, Gaskell and Neville 2013; Liu *et al.* 2011) and the wettability (Cheong, Gaskell and Neville 2013; Zhao *et al.* 2005; Bargir *et al.* 2009; Förster and Bohnet 1999;

Azimi *et al.* 2014; Herz, Malayeri and Müller-Steinhagen 2008a; Rankin and Adamson 1973a)), kinetics of crystallization and surface deposition (Crabtree *et al.* 1999; Kitamura 2002; Yu *et al.* 2004; Dyer and Graham 2002; Peyvandi, Haghtalab and Omidkhah 2012), and the induction time (Geddert, Augustin and Scholl 2011; Geddert *et al.* 2009; Jaouhari *et al.* 2000; Gabrielli *et al.* 2003) for surface scaling which is dependent on the flow regime (Han *et al.* 2006; Alahmad 2008; Vazirian and Neville) and the saturation rate (Merdhah and Yassin 2009).

Surface deposition and bulk precipitation are interlinked processes. However they have very different kinetics (Eroini *et al.* 2013). In an oilfield, the type of scale that deposits on the surface would be different from place to place i.e. the mechanism of scale deposition on the surface in the downhole region would be different from that on ground level components due to (a) the difference in water composition and saturation ratio between these two regions, and (b) the formation of crystals and particles in the brine solution while being transported to the ground level valves and pipe components. In so many studies (Wang, Neville and Meredith 2005; Cheong *et al.* 2008; Quddus 2002; Quddus and Al-Hadhrami 2009; Quddus and Allam 2000; Morizot, Neville and Hodgkiess 1999; Neville and Morizot 2000), the hydrodynamic effects on the process of scale formation on the surface have been surveyed as one mechanism referred to as "deposition" on the surface. In the presented work, the scale deposits on the surface are divided into two mechanisms: a "deposition process" which refers to the process of heterogeneous nucleation and growth at the asperities of the surface and an "adhesion process" which refers to the sticking of pre-existing crystals which have nucleated in the bulk solution and which build up as a layer on the surface. This paper assesses the effect of hydrodynamics on both processes and the relative scaling tendencies for a range of commercially-available coatings.

3. Experimental methodology

3.1. Substrates

A standard austenitic stainless steel (UNS S31603) is selected as a metallic reference material. The stainless steel samples are coated with sixteen different surfaces commercially-available types of coatings which cover a variety of surface roughness and surface energy surfaces with different surface compositions, as shown in Table-1.

Table 1- Modified substrate with their corresponding coating code

Coating Type	Coating code	Type details
Glass Ceramic	S-1	SiO_2–organic components
Paint	P-1 - P-5	Epoxies
Fluoropolymer	F-1 - F-5	PTFE, ETFE, PFA, FEP
DLC	D-1 - D-2	a-C:H
Ceramic	C-1 - C-3	TiN, CrN, CrN-Ag

3.2. Reagents

The water composition of the tested brine is derived from the real conditions of oil wells provided by Petrobras. As shown in Table-2, the supersaturated brine used in the study is composed of two complex brines. These were prepared separately by weighing the appropriate quantity of salts and mixing with distilled water, and then mixed with the ratio of 1:1, as follows:

Table 2- Brine composition of the scaling solution

Brine Solution 1		Brine Solution 2	
Salt	**Mass(g/l)**	**Salt**	**Mass(g/l)**
Na_2SO_4	1.6604	KCl	9.4228
NaBr	2.6372	$CaCl_2$	63.9039
$NaHCO_3$	0.1598	$MgCl_2$	13.1506
NaCl	228.0267	NaCl	180.8250
$NaCH_3COO$	0.0741	$BaCl_2$	0.4772

Both brine solutions were filtered by a membrane with pore size of 0.45µm. Before mixing the two brine solutions, they were heated up to 56°C and the "brine solution 1" was buffered by CO_2 to pH of 6.7. CO_2 buffering would be continuous during the whole scale tests to maintain the level of pH at a constant level throughout the experiment. The initial saturation ratio, were evaluated using the Multiscale® software, data are summarized in Table-3. There is a hydrodynamic tendency for scale formation of calcium carbonate, barium sulphate and strontium sulphate on the surface.

Table 3- Saturation Ratio of different inorganic scales at 56°C

Species	Theoretical initial Saturation Ratio
$CaCO_3$	10.1378
$BaSO_4$	121.7666
$SrCO_3$	3.7794
$SrSO_4$	11.7175

3.3. Surface Characterisation

Prior to any surface scale deposition tests, the surfaces need to be characterised in order to quantify their surface roughness and surface energy. The surface roughness measurements of each substrate are done by a Taylor Hobson surface profiler. Surface roughness refers to the irregularity of the surface texture formed by peaks and valleys, and the quantity of R_a is referred to an arithmetic mean of the absolute departure of the roughness profile from the mean line, as shown for each substrate in Table-4.

Table 4- Surface roughness of different coatings (surface roughness order: smooth to rough)

No.	Coating	R_a (µm)	No.	Coating	R_a (µm)
1st	**S-1**	**0.094±0.009**	10th	**P-5**	**0.799±0.051**
2nd	**C-2**	**0.104±0.009**	11th	**F-2**	**0.976±0.042**
3rd	**SS**	**0.109±0.005**	12th	**P-2**	**1.032±0.145**
4th	**C-3**	**0.136±0.010**	13th	**F-3**	**1.066±0.372**
5th	**D-2**	**0.138±0.017**	14th	**F-4**	**1.185±0.075**
6th	**C-1**	**0.142±0.012**	15th	**P-3**	**1.481±0.206**
7th	**D-1**	**0.152±0.040**	16th	**F-1**	**1.805±0.050**
8th	**P-1**	**0.351±0.074**	17th	**F-5**	**5.248±0.375**
9th	**P-4**	**0.685±0.206**			

Contact angle measurements of each substrate were performed by the sessile drop method which measures the contact angle of a series of liquid probes on solid substrate. The contact angle measurement tests are performed in an open air condition at a room temperature of 20°C, a relative humidity of approximately 40%. The liquid probes used are ultrapure water (18 MV) and diiodomethane; and their corresponding surface tension components are shown in Table-5.

Table 5- Surface tension (mN/m) components of liquid probes(Van Oss 2006).

Liquid	Total surface tension (mN/m)	Dispersive	Polar	Acid	Base
Water	72.8	21.8	51.0	25.5	25.5
Diiodomethane	50.8	50.8	0.0	0.0	0.0

The dispersive and polar components of surface energy calculations are based on a two component model for solid surface energy referred as Fowkes theory (Fowkes 1964), as follows:

$$\gamma_i(1+cos\theta_i) = 2\left(\sqrt{\gamma_i^d\gamma_s^d} + \sqrt{\gamma_i^p\gamma_s^p}\right) \quad i = 1,\ 2 \tag{1}$$

$$\gamma_s = \gamma_s^d + \gamma_s^p$$

$$\gamma_i = \gamma_i^d + \gamma_i^p \qquad i = 1{,}2$$

Where θ_i is contact angle of testing drop, γ_i^d and γ_i^p are dispersion and polar energy of testing drop i, and γ_s^d and γ_s^p are dispersion and polar energy of testing surface. The contact angle measurements of each liquid probe along with their corresponding surface energy components for different type of coatings are shown in Table-6.

As shown in Table-4, the smoother surfaces belong to glass ceramic, ceramic and DLC coatings while the fluoropolymers and epoxies have a higher relative surface roughness. On the other hand, as shown in Table-6, the surface energy of the fluoropolymers are relatively lower compared to the other types of coatings.

Table 6- Contact angle measurements and surface energy calculations of different liquid probes on tested coatings (surface energy from low to high)

Name	Diiodomethane (θ °)	Water (θ °)	Dispersive (mJ/m^2)	Polar (mJ/m^2)	Total (mJ/m^2)
F-3	82.15	106.66	16.41	0.97	**17.38**
F-5	79.71	112.63	17.64	0.15	**17.79**
P-4	83.05	94.63	15.96	4.30	**20.26**
F-2	78.99	96.44	18.01	3.07	**21.08**
F-1	78.93	92.69	18.06	4.33	**22.39**
S-1	72.23	102.96	21.63	0.83	**22.46**
F-4	71.50	102.83	22.04	0.80	**22.84**
P-3	73.39	87.24	21.00	5.51	**26.51**
C-2	63.51	82.11	26.56	5.89	**32.45**
SS	63.43	73.61	26.60	10.01	**36.61**
D-1	53.65	80.20	32.21	5.08	**37.29**
C-3	54.33	79.43	31.83	5.49	**37.32**
D-2	49.51	76.88	34.55	5.82	**40.37**
C-1	65.46	65.34	25.44	15.42	**40.86**
P-1	55.71	67.94	31.04	11.35	**42.39**
P-5	59.62	63.89	28.80	14.68	**43.48**
P-2	47.78	65.62	35.67	10.87	**46.54**

3.4. Dynamic scale deposition tests

The scale process depends on parameters such as pressure, temperature and fluid flow. The latter two conditions can be adjusted in the lab equipment using the Rotating Cylinder

Electrode (RCE) apparatus. The RCE equipment consists of an electrode rotator and a control unit which can control the rotational speed of the electrode in the vessel. The coupon is mounted on the tip of the shaft between two Teflon based rings which are chemically and electrically inert. The sample used in the static batch jar test is cylindrical with the diameter of 12mm and the height of 10mm.

Reynolds number is a dimensionless quantity which expresses the flow regime. This quantity is the ratio of inertial forces to viscous forces. In such setup, the Reynolds number will be calculated to determine the shear stress at the vicinity of the surface. Reynolds number of the rotating cylinder electrode with outer diameter, d_{cyl} (cm), can be computed as:

$$Re = U_{cyl}.d_{cyl}.\rho/\mu \quad (2)$$

where, U_{cyl} (cm.s^{-1}) is the linear velocity, ρ is the solution density (g.cm^{-3}) and μ is the viscosity of the solution (gr.cm^{-1}.s^{-1}). The linear velocity at the outer diameter (i.e. surface velocity) can be calculated as:

$$U_{cyl} = \pi.d_{cyl}.F/60 \quad (3)$$

where, F is expressed by rpm.

Hydrodynamic conditions can be predetermined using the RCE at different rotational velocities to have turbulent flows. Consequently different shear stresses at the vicinity of the surface. The shear stress on the cylinder surface can be calculated as follows(Gabe 1974):

$$\tau_{cyl} = 0.0791\rho Re^{-0.3}U_{cyl}^2 \quad (4)$$

where, τ_{cyl} is the shear stress (g.cm^{-1}.s^{-2}) at the vicinity of the surface. The unit of shear stress is normally expressed as Pascal, so:

$$1Pa = 1\frac{N}{m^2} = 1\frac{kg}{m.s^2} = 10\frac{g}{cm.s^2} \quad (5)$$

The sample was rotating in the brine at two rotational speeds: (a) 2000 rpm (Re~17,800) which represents the fully turbulent flow regime and (b) 20 rpm (Re~178) which represents the laminar flow regime for 90 minutes. The test results are then calculated as shown in Table-7.

Table 7- Hydrodynamic conditions of RCE test cases

Rotational Speed F (rpm)	Surface Velocity U_{cyl} (cm/sec)	Reynolds Number	Surface Shear Stress, τ_{cyl} (Pa)
2000	125.6	17845	7.851
20	1.256	178	0.003

3.5. Types of Methodology

The work has focused on an initial assessment of the antiscale properties of the samples with different coatings in an environment with the possibility of forming calcium carbonate, barium sulphate and strontium sulphate scales. The surfaces have been tested using a bulk jar test where precipitation occurred at 56°C and at atmospheric pressure. Two scenarios are designed to perform the dynamic scale tests, as follows:

- In scenario-1 (or adhesion process), the sample was immersed in the batch vessel, where the crystals are already formed into the mixed brine. The mixed brine is kept at 56°C for 90 minutes which is enough time for the system to equilibrate (as plotted in Figure 8). This test measures how the presences of pre-formed crystals from the turbid solution form on the surface. It assumes that adhesion dominates and deposition is minimal.
- In scenario-2 (or deposition process), as soon as the anions and cations are mixed, the sample is immersed into the brine for 90 minutes. As such there is a high driving force for heterogeneous nucleation which can occur at the surface asperities. The deposition can occur by growth of scale at these asperities. So the sample would be in the beaker during the crystallisation.

After each test, the sample was rinsed with distilled water and dried by compressed air and put in an oven. Repeated measurements have showed the ability of the polymer coatings to uptake liquid within themselves after the tests. McKeen (McKeen 2006) has reported that the water absorption of fluoropolymer, such as FEP, PFA and ETFE within 24 hours are around 0.01%, 0.03% and 0.03% by weight, respectively. In order to obtain the scaling tendency, the samples were weighed before and after an experiment with a mass balance having a resolution of 0.001mg in a controlled condition room with the temperature of 21°C and the relative humidity of 42%. Typically, two coupons were tested for each type of surface but in the cases where the results were different, a third coupon to experiment was done for each surface.

3.6. Measuring the turbidity

A Hach DR/890 Colorimeter was used to measure the turbidity of the scaling solution as the anions and cations were mixed. The calorimeter acts by measuring the reduction of light as it passes through the sample column of water and shows the results as Formazin Turbidity Unit (FTU). The turbidity as a function of time of the solution is plotted in Figure-1. The induction time for such a solution is so fast due to the high super saturation index that can be neglected. The turbidity increases rapidly in the first 10 minutes, and after some fluctuations, it is stable. As shown in Figure-1, the “deposition” test starts from minute “0”; and the “adhesion” test starts from minute “90” where the speed of the crystallization is in balance with the dissolution rate of the particles in the brine solution.

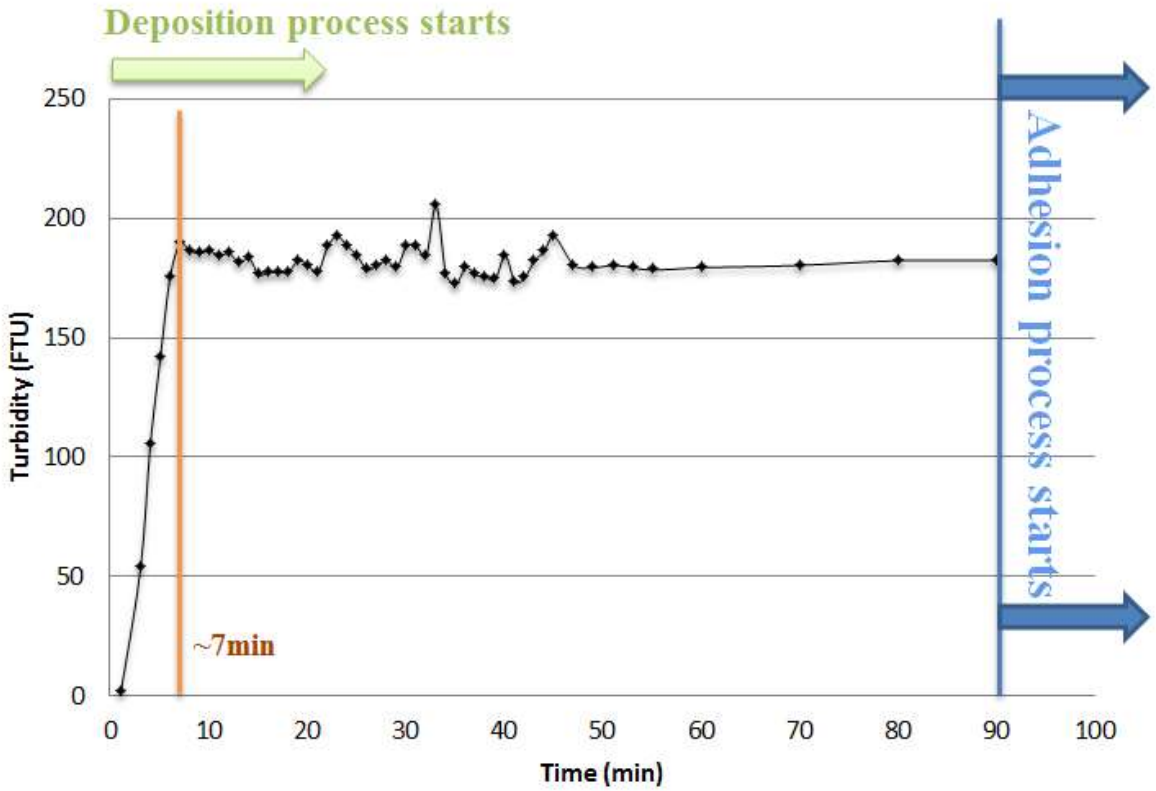

Figure 1- Turbidity measurements of the brine: "Deposition" test starts at minute 0 and "Adhesion" test starts at minute 90; the crystallization rate balances with the dissolution rate after around 7 minutes.

4. Results and Discussion

In an oilfield, as shown in Figure-2, the process of scale formation on the surface is different from one region to another. For instance, the type of scale formation down in the wellbore is different to that formed on the surface of valves and pipes at topside level. The main reason is due to the time that it takes for the bulk (or brine solution) to travel from downhole to topside level. Normally, in the downhole areas depending on the induction time of the fluid the number of particles found in the fluid is lower compared to the ground level. As a result, the process of scale formation dominantly occurs as heterogeneous nucleation and crystal growth on the surface (region A in Figure-2); while at the ground level, due to the time interval, the crystals are already formed in the bulk and the process of scale formation occurs mainly as the adhesion of the so called pre-precipitated crystals on the surface (region B in Figure-2).

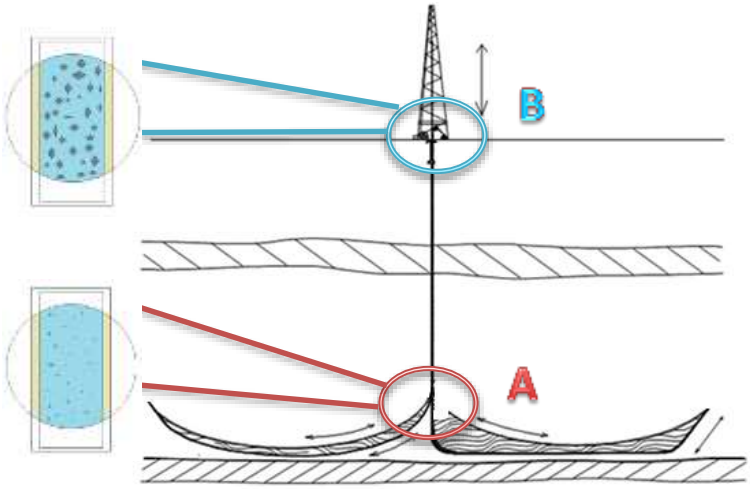

Figure 2- Schematic of scale formation in different regions of an oilfield: region A: heterogeneous nucleation and crystal growth, and region B: adhesion of particles to the surface

To replicate these conditions in the laboratory we have proposed two different scenarios, as scenario-1 (adhesion process) and scenario-2 (deposition process).

4.1. Mass Gain

Adhesion Process: The measured mass gain values on different modified surfaces are shown in Figure-3 and Figure-4, for two scenarios in both laminar and turbulent conditions. As shown in Figure-3, the mass gain for the adhesion process in the laminar flow regime ranges from 0.171mg to 1.227mg, while in the turbulent flow regime the mass gain ranges from 0.139mg - 1.898mg. In such tests, the mixed brine solution was kept for two hours before the insertion of the coupons into the brine solution. From the turbidity measurements after two hours it would appear that the rate of the dissolution and the rate of crystallization are in balance and the turbidity remains constant.

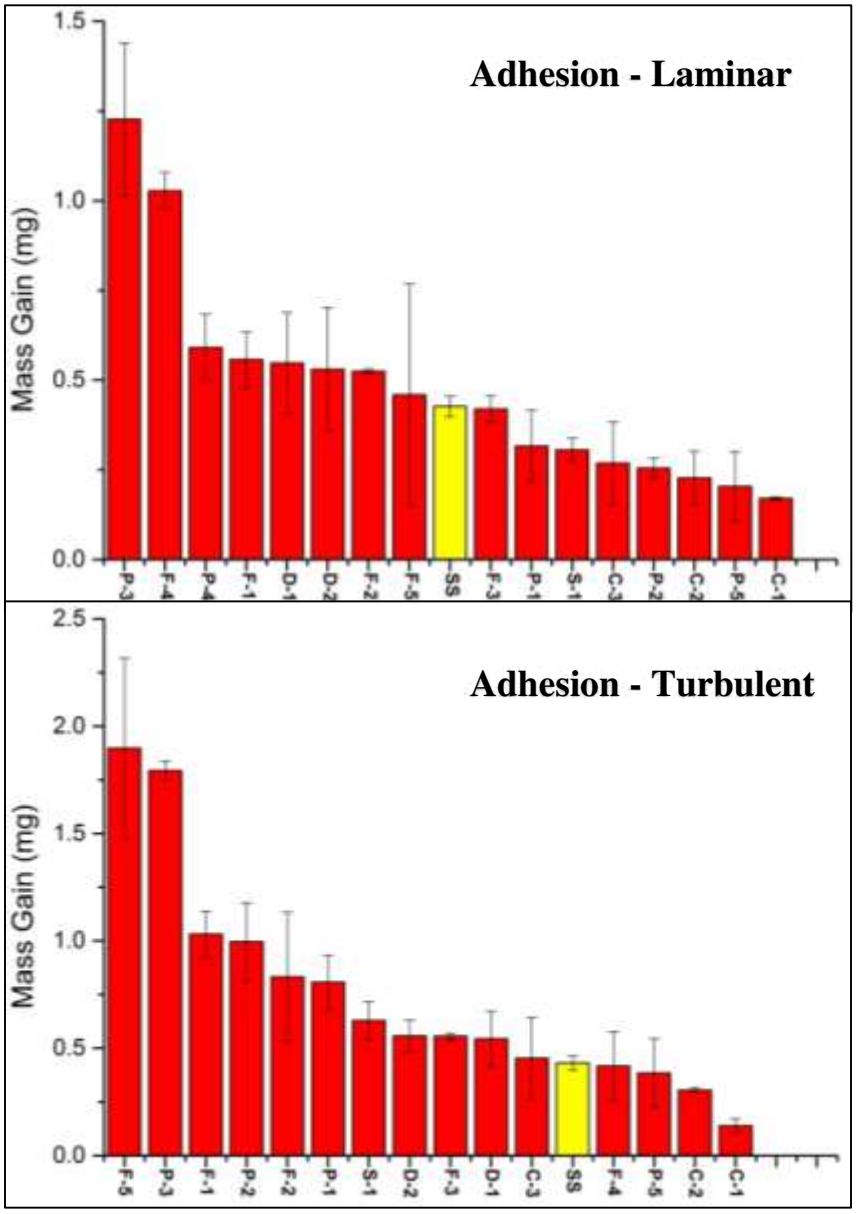

Figure 3- Mass gain of different type of coatings in adhesion tests, where focus is on adhesion of pre-precipitated of scale crystals. Yellow column is the stainless steel reference.

Deposition process: The mass of scale on the surface is consistently higher for deposition tests compared to adhesion tests. The mass gain for the deposition process in laminar conditions ranges from 0.430mg to 1.245mg, while in turbulent conditions the mass gain ranges between 0.693mg and 3.255mg, as shown in Figure-4. In deposition tests, when the coupon is immersed into the brine solution, the saturation ratio is at its highest rate initially and then progressively decreases during the test.

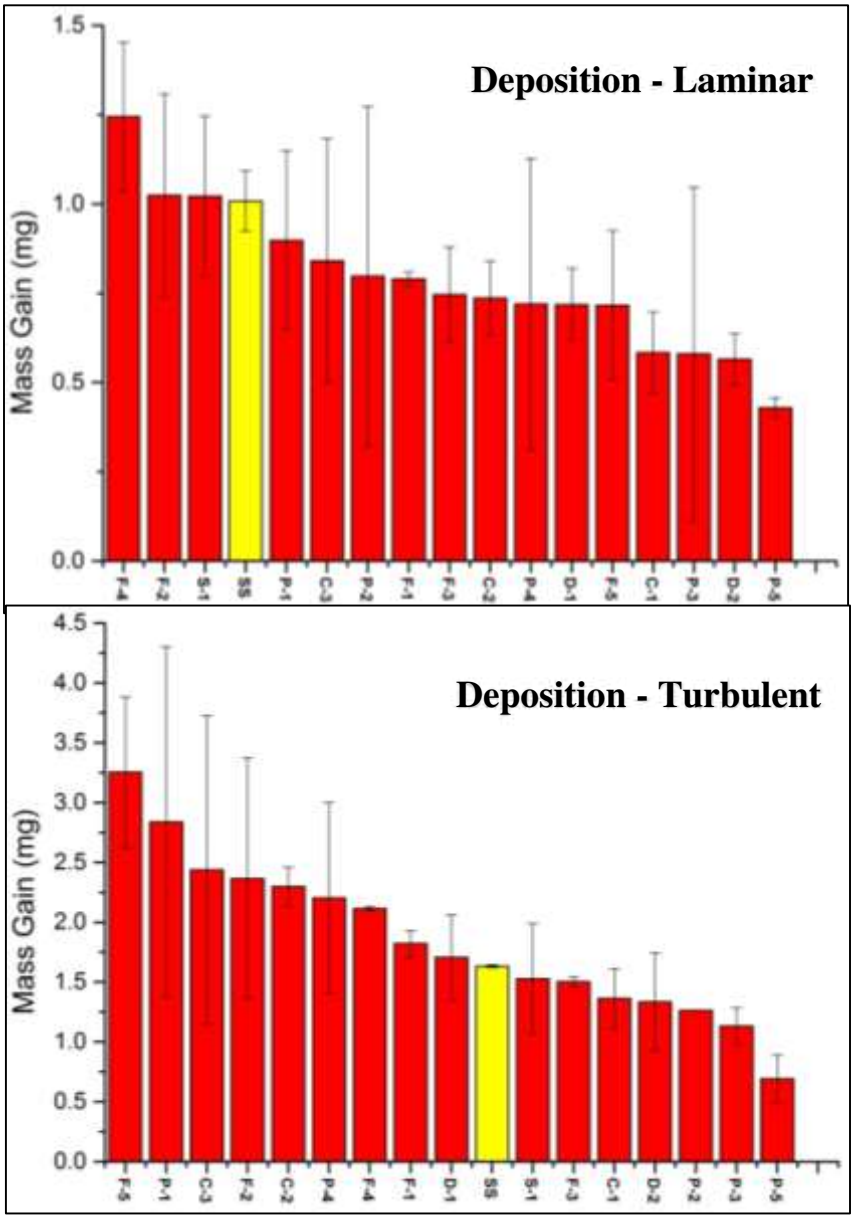

Figure 4- Mass gain of different types of coatings in deposition tests where the focus is on heterogeneous nucleation and crystal growth. Yellow column is the stainless steel reference.

One of the fluoropolymer coatings coded as "F-5" appears to have unique scaling characteristics among the other coatings. It is the roughest coating, whilst being the most hydrophobic. There is a trade-off between these two parameters in surface scale formation phenomena. The turbulent conditions for both the adhesion and the deposition tests, this type of coating has the worst performance while in the laminar conditions; it has a relatively good performance. In laminar condition, where mass transfer mainly occurs due to diffusion, hydrophobic effects appear to have a larger effect on hindering the scale formation on the

surface while in turbulent conditions such effects are negligible compared to surface roughness which increases the rate of surface scale formation.

It has been shown in many studies (Quddus and Allam 2000; Quddus 2002; Quddus and Al-Hadhrami 2009; Johnston, Taylor and Sutherland 2013) that the level of agitation (or hydrodynamic conditions) would affect the rate of scaling for all types of scale. In laminar conditions, the mass transport is mainly controlled by diffusion, while in turbulent conditions it is controlled by advection. Advection (or convection) has a higher effect on the scale formation on the surface compared to diffusion; which is in agreement with our both adhesion and deposition test results.

As shown in Figure-5, generally there is a higher rate of mass formation in turbulent conditions compared to laminar conditions in both adhesion and deposition processes. It can be explained as in the deposition process due to the higher rate of mass transfer the heterogeneous nucleation sites are more exposed to active ions, to form scale and grow on the surface.

However, the changes in the adhesion process are not as noticeable as in the deposition process which can be explained due to the mechanism of scale formation on the surface. In the adhesion process, due to the size of the pre-crystallised particles, the effect of momentum is significant. In turbulent conditions, there is a competition between the settlement of the particles and their adhesion to the surface (which favours scale formation) and the effect of momentum and shear stress induced by the brine to the particles to detach them from the surface (which reduces scale formation). As a result there is lower possibility for particles to settle and adhere to the surface in turbulent conditions. As the level of agitation rises to a critical point, the detachment forces (critical shear stress) exceeds the adhesion forces which results in self-cleaning or removing the scale deposits on the surface by hydrodynamic effects.

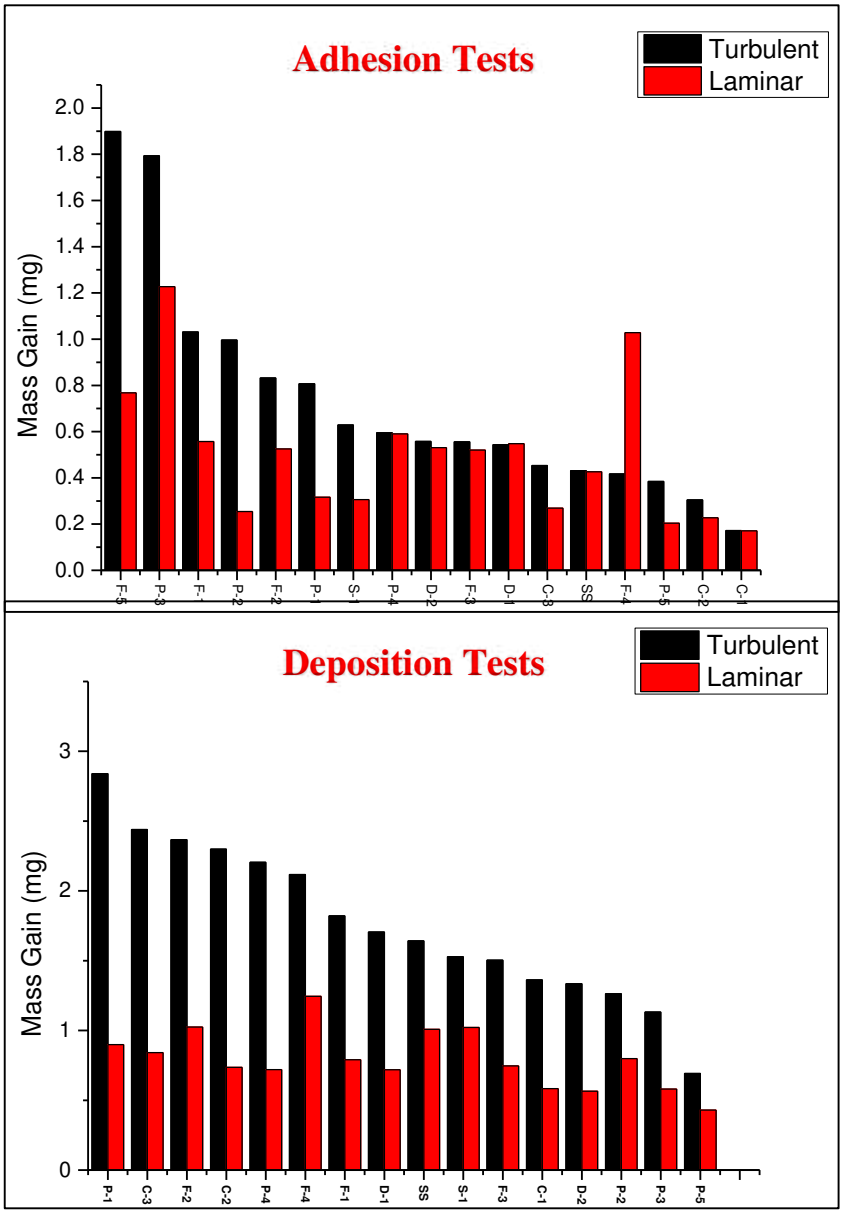

Figure 5- Comparison of scale mass gain in different level of agitation in both adhesion and deposition processes

As shown in Figure-6, the rate of scale formation on the surface is higher for deposition tests compared to adhesion tests in both laminar and turbulent conditions. As a result, more of the scale on the surface is due to a heterogeneous nucleation and crystal growth process rather than the adhesion of pre-precipitated particles to the surface.

One of the epoxy coatings, “P3”, has a distinctive behaviour in both flow regimes, having higher rates of scale formation on the surfaces in the adhesion tests. Such occurrence can be explained by its particular topography, i.e. the presence of lumps (e.g. rigid silicon carbide

particles) on its surface result in the escalation of the effect of particle adhesion to the surface.

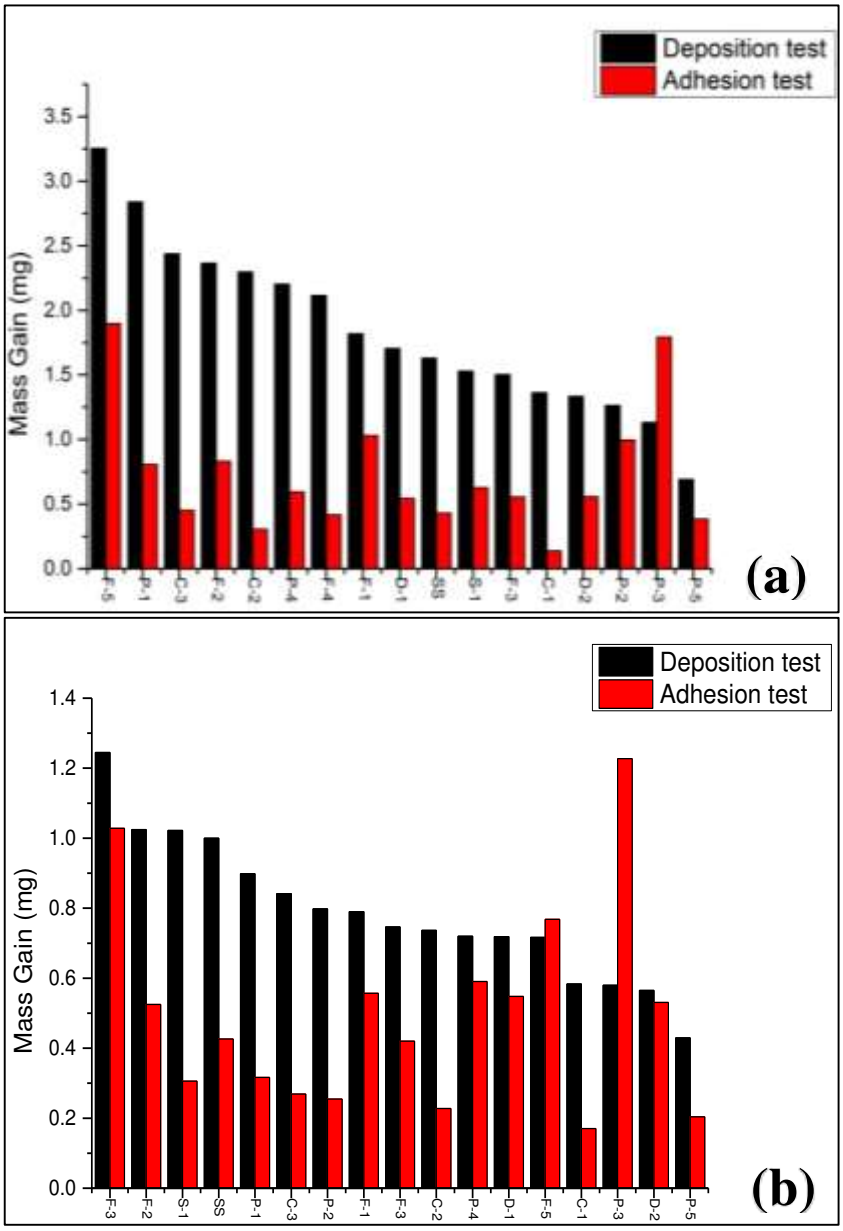

Figure 6- Comparison of different mechanism of scale formation in (a) Turbulent and (b) laminar flow conditions

4.2. Scale Control at Surfaces

In general, the parameters such as surface chemistry, surface roughness, surface energy and surface hydrophobicity are known as the criteria that play a major role in the scale formation process. However, it is not fully understood how each of these parameters affect the scale process.

For instance, low surface energy is known as one of the parameter which can decrease the scale deposition rate on a surface. However, Forster et al. (Förster and Bohnet 1999) showed that the deposition rate on a PTFE substrate coating is higher than for a DLC coating, although the latter has higher surface energy. Eroini et al. (Eroini *et al.* 2011) surveyed surface resistance to scale over a diverse range of substrates and reported that there is no strong correlation between the surface roughness/hydrophobicity and the scaling deposition. Rankin and Adamson (Rankin and Adamson 1973b) mentioned that roughness increases contact surface area; therefore, a rougher surface has a greater effective surface energy comparing to a smooth surface, and as a result a stronger adhesion can occur on rough surfaces. Keysar et al. (Keysar *et al.* 1994) tested the effect of roughness (0.1µm - 24µm) of mild steel under well-controlled conditions on calcite scale formation. They found that the adhesion force of rough surfaces is much higher than that of smooth surfaces. Herz et al. (Herz, Malayeri and Müller-Steinhagen 2008b) also conducted scale deposition tests on substrates with roughnesses ranging from 0.18µm to 1.55µm and reported that as the surface roughness increases the deposited scale enhances on the surface is increased. They reported that such behaviour can be attributed to the reduction of local shear forces at the valleys and the increase in primary heterogeneous nucleation rate on the surface. The key aspect appears to be the range of roughnesses and in such cases the surfaces with different roughnesses are all classified as "smooth". However, Cheong (Cheong, Gaskell and Neville 2013) reported that rougher surfaces do not necessarily end up with higher scale deposits. The author indicated that in polymer surfaces the roughness effects were found to be of secondary importance and other characteristics such as surface chemistry and surface energy could be more important.

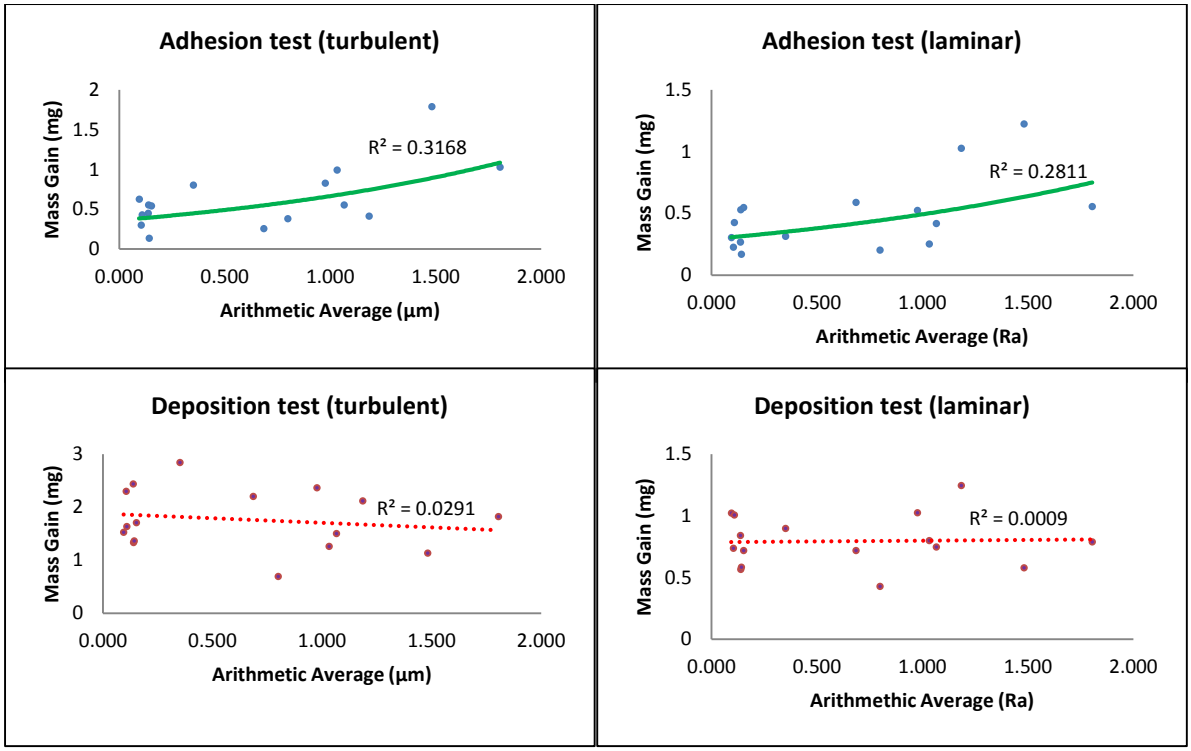

Figure 7- The effect of surface roughness on the scale mass gain for both adhesion and deposition tests

The roughness of the majority of tested coated surfaces ranges from 0.094µm to 1.805µm, except the coating "F-5" with a roughness of 5.248µm. Due its particular roughness, the coating "F-5" is excluded in Figure-7 to be assessed separately. As shown in Figure-7, the effect of surface roughness on the scale mass gain on the surfaces is assessed separately in both adhesion and deposition processes for both turbulent and laminar conditions. In the deposition tests, there is no noticeable correlation between the surface roughness and the scale mass gain, while in the adhesion process there is an apparent trend of increased mass gain with roughness but the correlation is very weak.

Surface energy is often quoted as a parameter which when it is increased on the surface would have an enhanced rate of scale formation on the surface. The deposition/adhesion test results are plotted in Figure-8 and the weak trend of reduced scale with increases surface energy seems to oppose the literature and conventional thinking. However, it is important to remember that there are many more variables here other than surface energy.

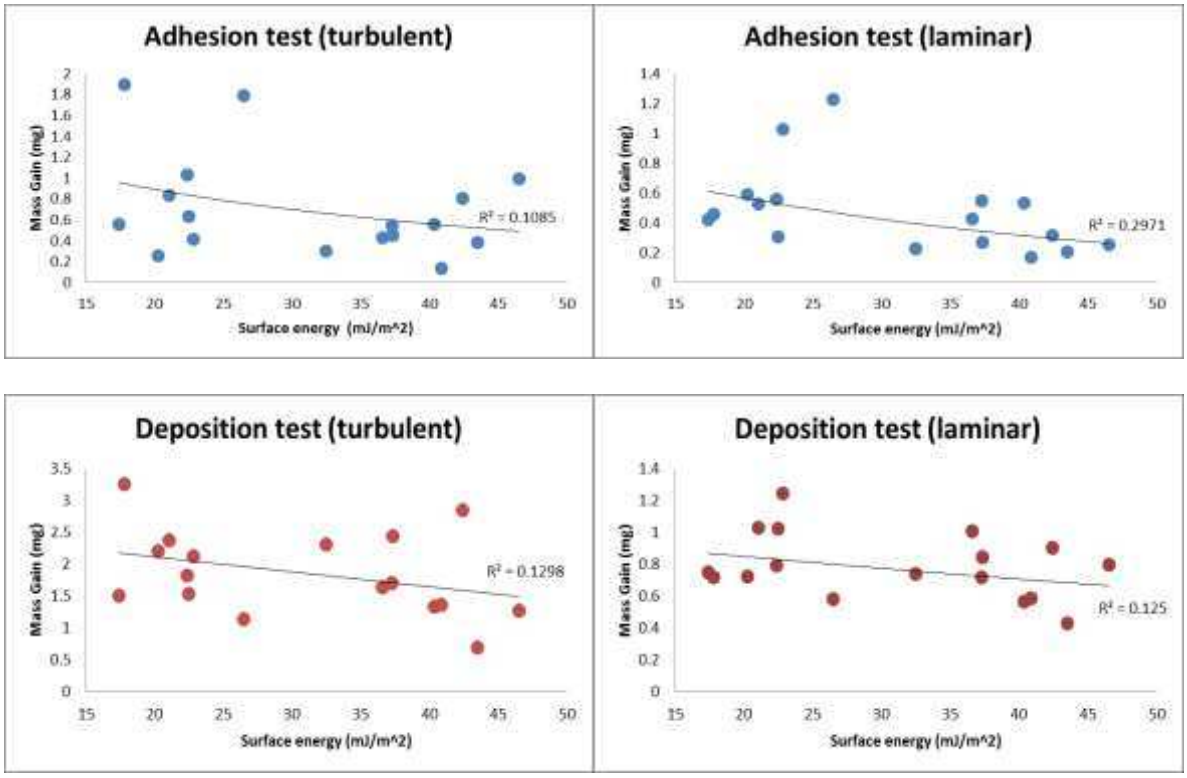

Figure 8- The effect of surface energy on the scale mass gain for both adhesion and deposition tests.

Surface energy and surface roughness show how they would behave in adhesion and deposition processes however these parameters along with surface chemical compositions are not the main factors affecting the scale formation on the surface.

4.3. Scanning Electron Microscopy (SEM)

As part of the qualitative assessment, scanning electron microscopy (SEM) has been applied to study the morphology of the crystals and the way that they are formed on the surfaces, as shown in Figure-9 and Figure-10 for both adhesion and deposition processes.

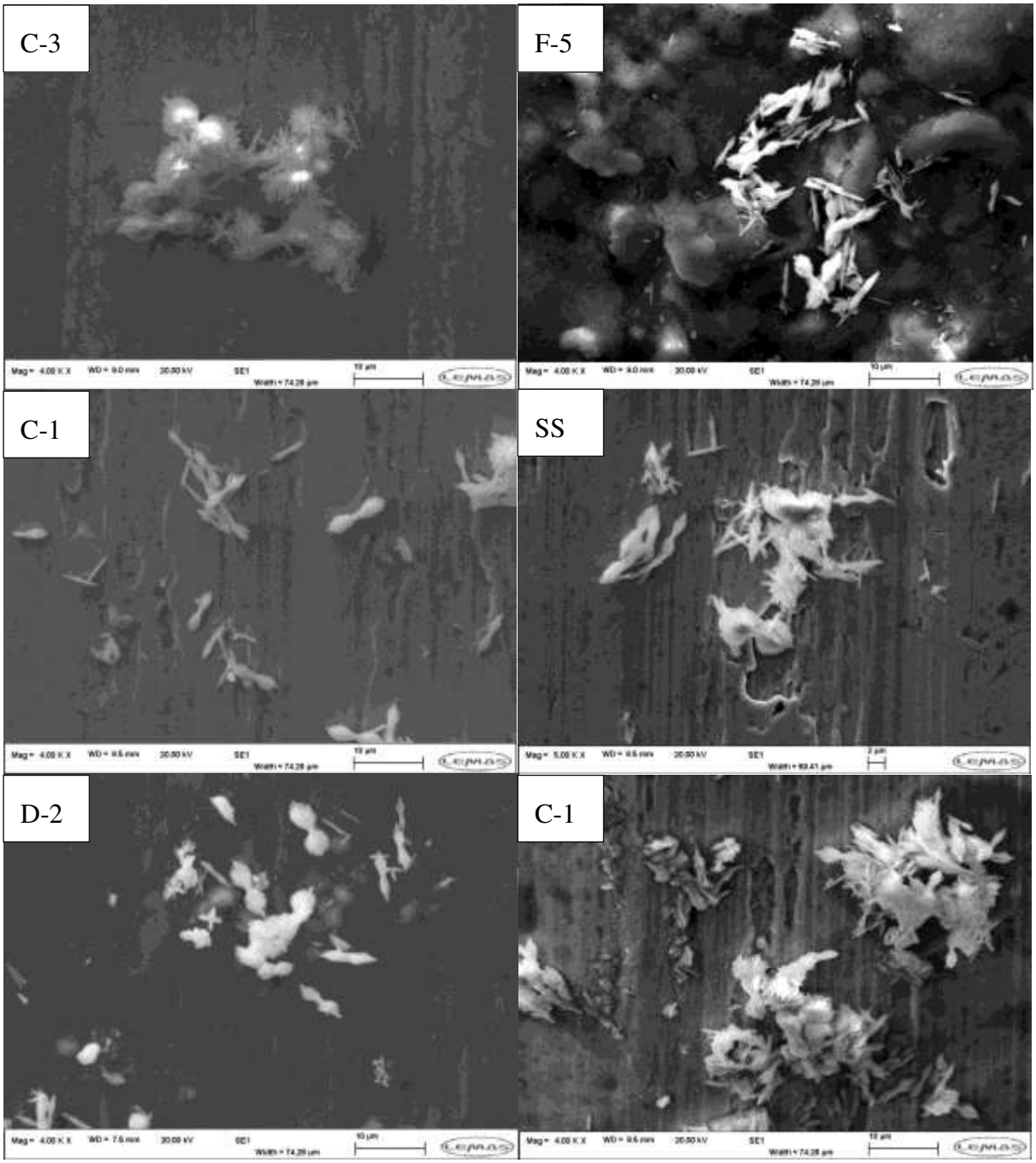

Figure 9- The SEM images of the scale deposits on different coatings in the adhesion tests: 1st column as laminar condition, 2nd column as turbulent condition.

As expected, the surface coverage by scale crystals in the deposition process is higher compared to the adhesion process; however, in terms of morphology there is no significant difference between the crystals formed on the surface in both processes neither in laminar conditions nor in turbulent flow regimes.

In all cases, the morphology of the majority of the formed crystals are shaped like a “bowtie”. The size reaches around 6-9µm in length and 1.5-2µm in width at both sides.

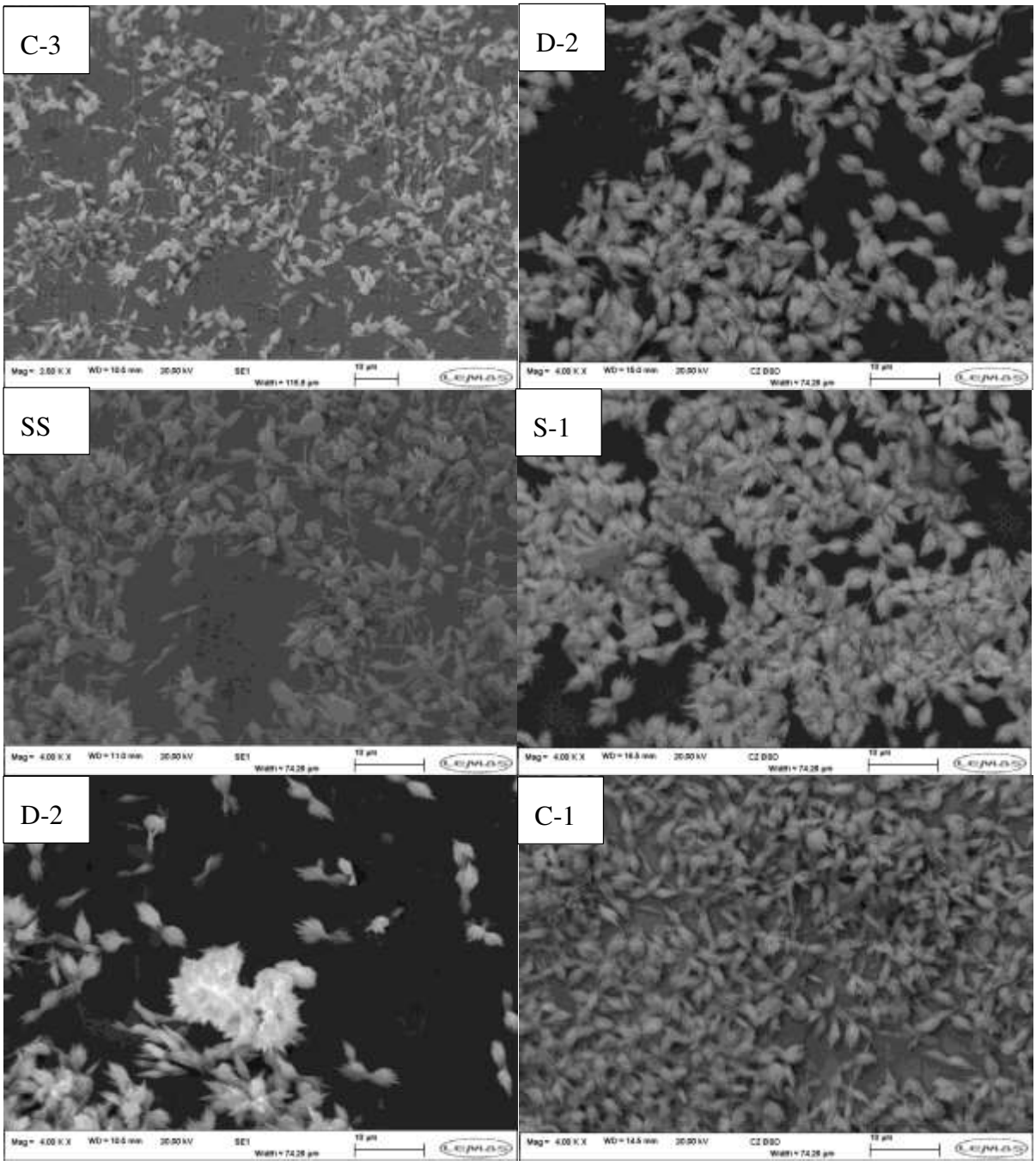

Figure 10- The SEM images of the scale deposits on different coatings in the deposition tests: 1st column as laminar condition, 2nd column as turbulent condition.

4.4. Inductively Coupled Plasma (ICP)

To understand more about chemical composition of the deposited crystals on the surface, the Inductively Coupled Plasma (ICP) spectroscopy technique is employed to measure the

relative amount of calcium, barium and strontium by mole percentage by dissolving the formed scale, as shown in Figure-11.

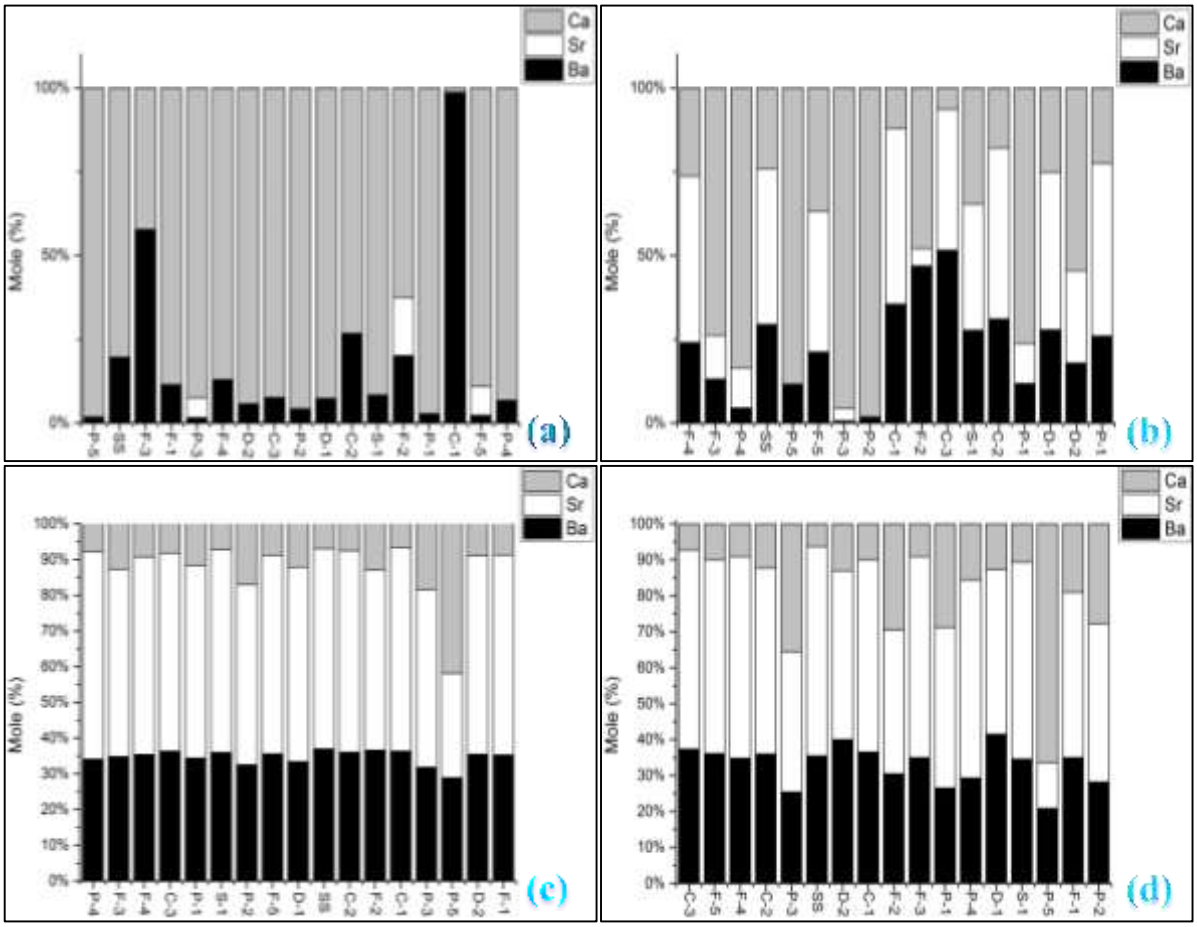

Figure 11- Mole percentage of calcium, barium and strontium existing on the surface as scale deposits in (a) Adhesion – turbulent, (b) Adhesion – laminar, (c) Deposition – turbulent and (d) Deposition – laminar.

As shown in Figure-11, in the adhesion tests calcium is the dominant ion present in the scale deposits on the surface, while in the deposition tests strontium and barium ions are more dominant. According to the DLVO theory, adhesion is determined by the balance between Van der Waals attractions and electrostatic double layer repulsion which is depending on the size, geometry and weight of the formed molecules(Oliveira 1997). In the deposition process, the attractive Van der Waals forces even for bigger and heavier molecules (e.g. $BaSO_4$ and $SrSO_4$) is predominant, while in the adhesion process the repulsive electrostatic double layer forces for heavy particulates are high enough to prevent the adhesion of scale deposits on the surface. Furthermore, due to the importance of the momentum and gravitational forces in the

adhesion process, it is easier for lighter scale crystals (e.g. $CaSO_4$ or $CaCO_3$) to adhere to the surface, while for heavier scale crystals formed by barium and strontium ions there are higher detachment forces. As a result, this trend is less obvious in the laminar flow regime compared to the turbulent condition due to lower critical shear stress induced by the brine to remove the crystal from the surface (Figure-11, comparing (a) and (b)). In terms of heterogeneous nucleation and crystal growth (deposition process), the hydrodynamic effects do not affect the chemical composition of the scale deposits, while the level of agitation would change the nature of scale deposits in the adhesion process.

5. Conclusions

The presented work surveyed the effect of the hydrodynamic conditions on the rate of inorganic scale of a wide range of industrial available coatings in a complex brine solution in two processes: heterogeneous nucleation and crystal growth as "deposition process", and the adherence of the pre-crystallised particles to the surface as "adhesion process". The key findings of this study are:

- An increase in the level of the turbulence in the bulk would increase the scale formation rate on the surface in both deposition and adhesion processes.
- The surface scale formation rate is more dominantly controlled by the heterogeneous nucleation and crystal growth rather than the adherence of the pre-crystallised particles; however, the level of agitation could have inverse effects on one process to another.
- The relative chemical composition of scale deposits would be affected by different mechanisms of scale formation on the surface (i.e. from the deposition process to adhesion process), while the morphology of the scale deposits hasn't changed.
- The results show that modifying some parameters (e.g. surface roughness or surface energy) cannot merely be a guarantee as a good antifouling parameter, and there should be a combination of factors chosen with regard to scale chemical composition, hydrodynamic effects, and the process of scaling to predict and prevent surfaces that are prone to inorganic scale.

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