

Scaling Assessment, Inhibition and Monitoring of Geothermal Wells

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ABSTRACT

The formation of inorganic, sparingly soluble salts from aqueous brines during geothermal energy production, is known as scale and it is one of the major flow assurance problems. The damage caused by scale is one of the biggest challenges encountered by geothermal industries. Scale deposition damages the downhole equipment and moreover decreases in flow rate leads to a loss in production. Scale forms and deposits under supersaturated conditions, wherever the mixing of the incompatible types of water, formation water from the bottom hole and the injected seawater, takes place. Or when temperature or pressure changes are severe enough to produce a supersaturated solution. The deposited scale adheres on the surfaces of the producing well tubing and on parts of water handling equipment, where it builds up in time and leads to problems in reservoirs, pumps, valves and topside facilities. The rapid increase of the mineral deposits leads to inevitable damage of the equipment parts. As a consequence, suspension of production activities is necessary for the recovery or replacement of damaged parts. The formation of scaling on the inner surface of casings depends on the scaling tendency of the water and the surface chemistry and morphology of the casing. Many mitigation strategies exist, the most common are: scale inhibitors and acids washes. The scaling tendency can only be lowered by a chemical intervention on the production fluids: reduce the supersaturation of the salts in the water by inhibitors that form chemical complexes with the scaling ions. Preferably, no scale inhibitors are used, and other ways of prevention are required. In this study we experimentally show how the amount of scaling that is deposited on a substrate mainly depends on three parameters: the surface energy of the casing and the roughness and the bulk modulus of its inner surface. A long term solution for scaling prevention is the implementation of a casing material that is intrinsically better resistant against scaling. A new class of pipes that shows intrinsically improved scaling performances is glass fiber reinforced composites. The inner surface of the pipes consist of the polymer matrix of epoxy or polyethylene and will have a different surface energy than steel pipes.

1. INTRODUCTION

The formation of inorganic, sparingly soluble salts from aqueous brines during oil and gas production, and during geothermal energy production, is known as scale and is one of the major flow assurance problems (University of Leeds). Scale forms and deposits under supersaturated conditions, wherever the mixing of the incompatible types of water; formation water from the bottom hole and the injected seawater, takes place. Or when temperature or pressure changes are severe enough to produce a supersaturated solution. The deposited scale adheres on the surfaces of the producing well tubing and on parts of water handling equipment, where it builds up in time and leads to problems in reservoirs, pumps, valves and topside facilities. Since the deposition/ adhesion takes place also in heat transfer equipment such as boilers and heat exchangers, a decrease in the performance during the heat exchange as well as in flow rates occurs. These problematic conditions are found not only in oil and gas fields but commonly also in geothermal plants where energy is obtained from hot fluids. The rapid increase of the mineral deposits leads to inevitable damage of the equipment parts and to a decrease of the production rate. As a consequence, suspension of production operations is necessary for the recovery or replacement of damaged parts and to remove the clog generated by the scale deposition. The total costs of scale (for the oil and gas market) has been estimated at USD 1.4 billion (Eroini, 2011).

Two common, most insoluble types of inorganic scale, are calcium carbonate (CaCO_3) and barium sulphate (BaSO_4). Both mineral types are undesirable since they result in blockage of pipes and in many other flow assurance problems. A very well-known case of scaling occurring near the wellbore is the formation of calcium carbonate when the pressure of the fluid drops and becomes lower than the bubble point of CO_2 . Thus CO_2 start degassing from the brine, resulting in pH increase and subsequently in an environment saturated with respect to CaCO_3 . Scaling can also occur when incompatible types of water (e.g. seawater and formation water) are mixed and forms insoluble salts (Mavredaki, 2014). Most of the research on scaling has been devoted to bulk phase scaling or on seeded crystals. Only during the last few decades more attention has been given to the growth of scaling directly on surfaces. Currently, it has been accepted that calcium carbonate reveals different growth kinetics in the bulk phase than the one dominating the deposition on a surface (Zhang, 2012). The formation of scaling on the inner surface of casings depends on the scaling tendency (supersaturation) of the water and the surface chemistry and morphology of the casing. Steel casings have been shown to be very sensitive for scaling, and many mitigation strategies have been proposed: coatings, scale inhibitors, acids washes etc. The scaling tendency can only be lowered by a chemical intervention of the production fluids: reduce the supersaturation of the salts in the water by inhibitors that form chemical complexes with the scaling ions.

The mechanism in the formation of scaling can be divided in several steps:

1. Scaling salts in water become supersaturated, due to mixing temperature and/or pressure changes, etc.
2. Inorganic salts start to precipitate around small crystallization nuclei.

3. The nucleus can be the surface of the pipe or a inhomogeneity in the liquid.
4. If the nucleus forms in the liquid and does not adhere to the pipe, the salt crystal will grow, but does not form scaling in the pipe.
5. If the nucleus is formed in the liquid, but is deposited onto the pipe, or the crystal is nucleated from the pipe wall, scale starts to build up.
6. Once the initial crystals have started to grow on the wall, further scaling will occur.

To properly manage the scale related issues, the formation of scale must be prevented in the nucleation steps: this must not start at the pipe inner surface. The nucleation stage of the scale can be influenced by the surface chemistry of the pipe. The most important parameter to be assessed is the surface energy of the material on which the scale is deposited. But also the morphology and roughness will play an important role.

A more long term solution would be the implementation of a casing material that is intrinsically better resistant against scaling. Thus has bulk chemical and physical properties that prevent the deposition of inorganic salts. A new class of pipes that may show intrinsically improved scaling performances is glass fiber reinforced composites. The inner surface of the pipes consist of the polymer matrix of epoxy or polyethylene and will have a different surface energy than steel pipes.

Although the scaling of metal pipes has been a topic for research for many years, the scale formation of polymer pipes (Wang, 2005) has not been extensively investigated yet. The majority of the literature describes the prevention of scaling by using scale inhibitors, or the mechanical removal of scale. In this study we performed several scale deposition experiments, both on steel and polymeric materials that can be used as wellbore casing.

2. METHOD

2.1 Theoretical background

The driving force for the inorganic scale to form is the saturation ratio (*SR*) or saturation index (*SI*). It is essential for reactive crystallization to occur that the *SR* is greater than 1, in the mixed solution.

$$SI = \log(SR) = \log\left(\frac{a_{Ca} \cdot a_{CO_3}}{K_{sp}}\right) \quad (1)$$

Where a_{Ca} and a_{CO_3} are the activities respectively of the Ca and CO_3 ions and K_{sp} is the solubility product. The adopted solution of K_{sp} is given by Larson (1942).

Since most scaling studies have only used thermodynamics and bulk kinetics to model scale formation, they have led to under or over estimation of the scaling. For accurate influence of the surfaces on scaling, surface effects must be taken into account, such as chemistry, pre-scaled surfaces and roughness. A study on the formation of scale on stainless steel revealed that at high *SR* values (>5) bulk crystallization is favorable and surface scale is much less than when $SR < 5$ (Eroini, 2011).

The activity of calcium and carbonate depends on the concentration, the temperature and the pressure. For low concentrations, the activity coefficient of ions (f_i) is given by:

$$\log(f_i) = \frac{-0.51 \cdot z^2 \cdot \sqrt{I}}{1 + \sqrt{I}} \quad (2)$$

Where z is the charge of the ion and the ionic strength (I) of the solution is given by:

$$I = \frac{1}{2} \cdot \sum C_i \cdot z_i^2 \quad (3)$$

Where C_i is the molar concentration of the i th ion present in the solution and z_i is the charge of the ions. The activity of each ion is now given by:

$$a_{ion} = f_i \cdot C_{ion} \quad (4)$$

Extensive research has shown scaling to be a two-stage process, with the first period identified as the induction period and the second period known as the fouling period (Bargir, 2007). During the induction period a small amount of scale (inorganic particulate fouling) accumulates on the surface without significantly affecting material performance. Although the quantity of scale formed is small, it is enough to condition the surface and enable a thin layer of scale to form. It is this conditioned layer which is succeeded by the fouling period, an overall decrease in the performance of the system. The induction period, while often neglected, offers much potential for mitigating fouling. The formation of a conditioning layer during the induction period is a balance between the deposition and removal of material at the interface between the solid and liquid. The deposition process is classically viewed as a heterogeneous nucleation process, where foreign bodies or impurities act as nucleation sites. The energetics of heterogeneous nucleation is described as a modification of homogeneous nucleation to account for the different interfaces and precipitation processes.

The interfacial tensions are composed of dispersive or Lifshitz-van der Waals, Lewis acid-base (or electron-acceptor/donor) and electrical double layer force. In a changing pH environment, the charges on the surfaces can change (especially in the case of metals and metal oxides), which leads to a change in surface tension due to the formation of electron/donor moieties. This will influence the adhesion significantly. The surface energy is constructed of at least two contributions: dispersive and a-scalar (combined dipolar, hydrogen bonding and induction forces) forces. For example metals have a significant a-scalar contribution, whereas fluorinated polymers do not. An important parameter that steers the adhesion of scaling crystals to a surface is the work of adhesion (Mitchel, 2010 and van Krevelen, 1997). Taking subscript 1 for the scale, 2 for the substrate and 3 for the water, the work of adhesion can be written as:

$$W_{adh} = \gamma_{13} + \gamma_{23} - \gamma_{12} \quad (5)$$

If this energy is large, then the scale prefers to be only in contact with water and the adhesion between scale and surface will be poor.

The lowest adhesion will be found if the interfacial tension between scale and surface is lower than the combined interfacial tension between scale-liquid and surface-liquid. Since the surface tension of water and calcium carbonate are more or less fixed, the surface energy between the substrate and scale crystals, γ_{12} , must be low to reduce adhesion between scale and surface.

The surface tensions as described above are only valid if the surface is completely smooth. Any roughness on the surface distorts the surface energy, because of an increasing contact area (Good, 1998). Good introduced the ratio r :

$$r = \frac{a}{A} \quad (6)$$

in which a is the real microscopic area and A the apparent area.

The apparent surface or interfacial energies between the rough surface and the scale, or the water increases with a factor r . The roughness of a surface can be characterized by several different roughness parameters, such as R_{rms} , (root mean squared) or R_a (arithmetic average). The ratio r can be estimated using the roughness root mean squared by:

$$r = \frac{R_{rms}^2}{\lambda^2} + 1 \quad (7)$$

In which λ is the distance between the peaks on the surface. So if the roughness increases, the apparent surface tension of the surface, γ_2 increases. And looking at the work of adhesions as was just described above, and increasing γ_2 results in a more positive work of adhesion, so more scaling. For the assessment of the influence of the roughness on the surface tension, two parameters for the roughness of the surface are needed.

Next to the influence of surface roughness on the interfacial tension of the scale and substrate, also the roughness of the substrate itself plays a significant role (Bargir, 2007). Height distribution is considered to be a major factor during adhesion between rough surfaces. When the scale is growing on a rough surface, the scaling is favored when the roughness is high. If, in that case, scale starts to grow, the adhesion may be poor and can be easily washed away.

2.2 Scaling experiments

To quantify the relevance of the parameters that mostly influence the deposition of scale on the inner surface of the casing we created a special experimental set-up. This was engineered as a result of the assessment of four literature tests: the quartz crystal microbalance (QCM) experiment (Eroini, 2011, Mavredaki, 2014), the bulk jar test (Carpentier, 2014, 2015), the flow cell (Eroini, 2011) and the dynamic flow rig (Mavredaki, 2014).

The QCM tests were performed to monitor the formation of scale on the steel surfaces and it was built into a flow cell.

In the bulk jar test scale cations and anions are heated up to 80°C and mixed together in a jar. The sample is immersed in the liquid and rotated to obtain laminar or turbulent flow. The scaling tests were performed for 2 hours, and the amount of scaling is measured by weighing the samples. Alternatively, only Calcium carbonate scale can be produced by using a simpler mixture at lower temperature of 50°C.

In the flow cell two components of brine are mixed in a jacketed beaker at elevated temperatures. The mixed liquid is pumped through a flow cell having windows to visually assess the growth of the scaling layer. A turbidity and pH meter monitor the change in liquid properties. Only calcium carbonate is monitored.

Since we will be assessing the difference between surfaces, and not the scaling tendency of solutions, not a single value for the saturation ratio (SR) is selected, but it is increased gradually during the test. A flow cell is more representative for down hole conditions, but is more difficult to construct and only a single sample per experiment can be measured. Furthermore, high volumes of scaling brines are required. The scaling must start after mixing, so sufficient induction time was allowed. This means that the saturation ratio (equation 1) at the point of injection of the second fluid into the first must not exceed a value of 20.

Finally, during the dynamic flow rig test the two brine solutions are mixed at elevated temperatures and forced through a stainless steel capillary cell. The pressure built-up over this cell due to the precipitation of calcium carbonate is monitored in time. Various saturation ratios were assessed between 54.8 and 2.5 for their scaling tendency. The induction time for scaling increases rapidly below a SR value of 4.

The scaling experiment that was performed in this paper will result in an initial assessment of the scaling tendency of several surfaces as a function of the coating properties, surface tension (γ), roughness (R), and modulus (E). The surface tension is varied by the incorporation of hydrophobic and hydrophilic groups in the coatings. The roughness variations are introduced by the implementation of nanotexturing on the metal substrate or on the coating surface by embossing. The modulus is varied by the use of different amounts of crosslinker in the same formulations or by using a different substrate, such as polymer composite. Different coating formulations were adopted to change the surface energy of the steel plates and are listed in Table 1.

Three steel substrates are used: Q-lab steel panels QD, R and S. These have different surface roughness. The surface modifiers and coatings were applied from a very dilute solution to the steel substrates using a 10 μ m doctor blade. Taking a volume fraction of 2 %, this would yield a 200 nm coating layer on the substrates. The surface modifiers, solvents and curing protocol are listed in Table 1.

Three different epoxy formulations have been included, because this could give qualitative and quantitative indications about the material properties that should be modified to improve the scaling behavior of glass fiber reinforced epoxy pipes.

The surface energies of all samples were measured using a Krüss DSA100 surface tension machine. The surface tension experiments were done on coated QD panels, because these had a smallest distortion from surface roughness. A droplet of water is placed on the

surface and the contact angle between the droplet and the surface is measured. This is repeated with a droplet of diiodo methane. From the contact angles, the dispersive and polar component of the surface energy can be calculated.

Type	Name	Solvent	Curing process
Fluorinated	Fluoroacrylate	2% in FC 770	Room temperature
	Fluorolink F10	2% in water/IPA	Room temperature
Epoxy	Araldite (2:1)	2% in toluene	60 min at 80°C, 15 min at 150°C
	Araldite (2:5:1)	2% in toluene	60 min at 80°C, 15 min at 150°C
	Araldite (2:1.5)	2% in toluene	60 min at 80°C, 15 min at 150°C
PDMS	Sylgard 184	2% in hexane	2 hours at 80°C
SiO ₂	Tetraethyl orthosilicate (TEOS)	2% ethanol	1 hour at 120°C
	SmartCoat	1% ethanol	Room temperature
Alkyl	TEOS/Decyl trimethoxy silane (DTMS) (1:1)	2% ethanol	1 hour at 120°C

Table 1. Surface modifiers and solvents used in the scaling experiments.

The roughness of the substrates is measured using a Sensofar Optical Imaging Profiler. An area of approx. 500x500 μm² is scanned using the confocal microscope. Using the processing software, the most relevant roughness parameters are determined, such as the average roughness (R_a), surface area increase, peak area (S_h) and dale area (S_d).

The scaling experiments are conducted as follows:

- The substrate is coated with the surface modifier
- Three polymer cylinders are glued on the substrate, two on top of the coated area, one on the uncoated steel (Figure 1)
- The cylinders are filled with 4 ml (0.1 M) CaCl₂ solution
- A 0.2 M solution (4 ml) of NaHCO₃ is added rapidly in the center of the cylinder. When the solutions are mixed in this way, the CaCO₃ will slowly starts to form after an induction period. This is needed to avoid the immediate crystallization of the scale in the bulk.
- The scaling solution is left for 1 hours at room temperature and the scale will form on the substrate.
- Then, the cylinders are removed and the substrates are thoroughly washed, to remove the unreacted chemicals, and scaling that is not formed on the substrates.
- After drying the scaling layers are characterized.
- The polymer tube on the untreated steel is used as reference measurement, and as a measure for the reproducibility of the scaling experiments.
- All experiments yield a duplo for the scaling tendency.

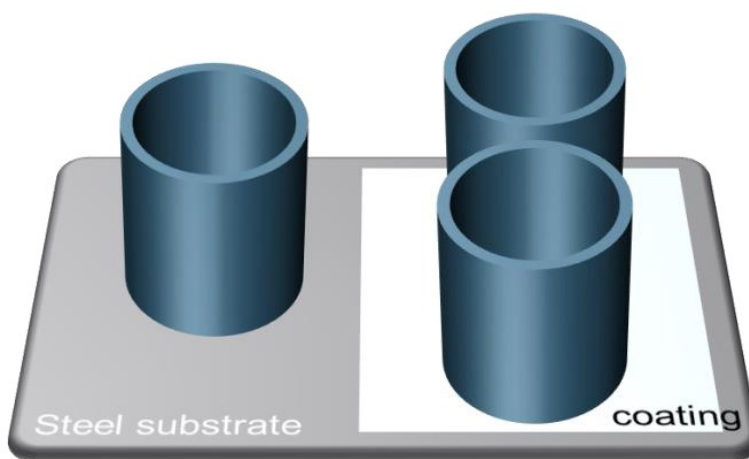


Figure 1. Scaling experiment set-up of three glued polymer tubes on the substrates.

After all scaling experiments were performed, a series of 30 steel substrates were obtained, all having a layer of scale formed in the polymer tubes. The polymer tubes were removed and the resulting scaling layers were characterized.



Figure 2. Large scaling experiments on 30 different substrate-surface modifier combinations. Left: overview. Center: samples during scaling. Right: samples after scaling.

The characterization of the scale formation is a very important aspect of the current project. Normally, the weight changes are monitored of samples that are introduced into scaling liquids. However, since we have only used small parts of the substrates for scaling, weight measurements are not sufficient. Therefore, the specular light reflection from the surface was monitored using an Ocean Optics USB 4000 spectrophotometer at 650 nm. The reflected light from the non-treated steel surface was used as reference, and the absorbance of the scaling layer was calculated according to:

$$A = -\log\left(\frac{I_{scale}}{I_{steel}}\right) \quad (8)$$

I_{scale} is the light intensity of reflected light from the scaling layer and I_{steel} is the reflected light from the steel substrate. First, the light reflection of the scale layer that was formed was measured, then the scale was removed by the application and removal of an adhesive tape. The forces generated in this removal were max 2.5 N/cm, but could also be close to 0 N/cm, when the scale was not attached to the substrate. When the scale was not firmly attached to the substrate, it came off and a cleaner surface was left behind. This was observed in a lower value of the absorbance. This experiment resulted in information about the adhesion between scale and substrate.

The scaling experiments on the glass fiber reinforced (GFR) epoxy tubing was done in a similar way as the steel samples. Some parts of the inside of the epoxy tubing were coated with the surface modifiers as described above. The same scaling experiments were done using the polymer cylinders glued to the inside of the tube. Some of the polymer cylinders glued on the inside of the GFR epoxy tube are shown in Figure 3. Each cylinder was filled with the scaling liquid and left for 1 hour, after which the liquid was removed and the ring was washed. Then, a new position in the tube was treated. After drying of the samples, similar light reflection experiments were performed as were done for the steel substrates.

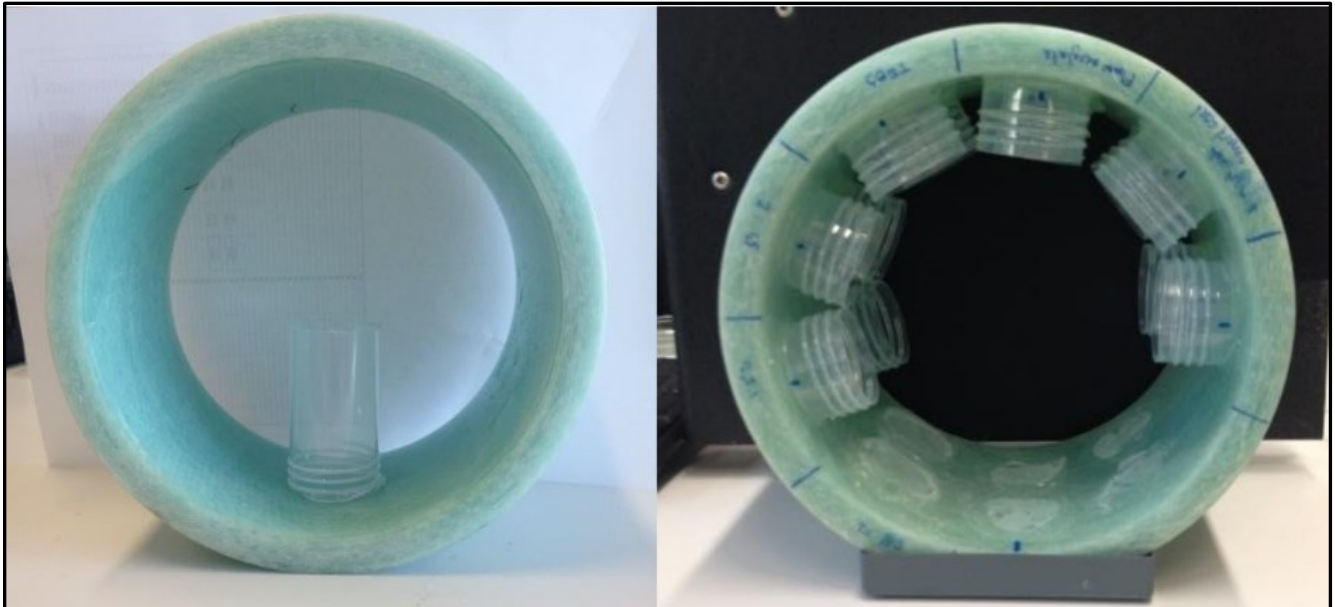


Figure 3. Scaling experiments on the inside of the Glass Fiber Reinforced epoxy tube.

3. RESULTS & DISCUSSION

The first series of experiments is conducted at 23 °C. The beaker is filled with a CaCl₂ solution of 0.05M, the CO₂ concentration is kept atmospheric (~300 ppm). A solution of 0.002 M NaHCO₃ is added slowly to the CaCl₂ solution. Using the equations above, a mixture of 0.05M CaCl₂ and 0.002M NaHCO₃ (1:1) has a SR value of 17. At the point of injection, a high NaHCO₃ concentration exist after which the NaHCO₃ is diluted into the rest of the liquid. However, due to mixing and dilution of the NaHCO₃ and CaCl₂ liquids the SR value will never exceed the 21. At the end of the experiment all the liquid has a SR of 17, although the reaction of the calcium with the carbonate will reduce the SR. During the experiment the HCO₃⁻ is converted to CO₃²⁻. The concentration of CO₃²⁻ is low compared to the concentrations of Ca²⁺ and HCO₃⁻. In the initial reaction of Ca²⁺ with CO₃²⁻ the consumed carbonate is replenished by the bicarbonate, and the concentration of carbonate remains rather constant: the SR value decreases only slightly. Once the amount of reacted calcium is equal to half of the added bicarbonate, the concentration of carbonate decreases orders of magnitude and the SR becomes almost zero.

Assuming that serious scaling will occur at SR values above 5, when adding NaHCO₃ to Ca, scaling will start only when half the (0.002M) NaHCO₃ is added to the (0.05M) calcium solution. On the other hand, when the calcium solution is added to the bicarbonate solution, the SR value is initially above 20 and stays this high almost to the end of the addition (Figure 4). This is caused by the fact that the ionic strength increases upon addition of the CaCl₂, and without calcium the carbonate concentration is substantially higher, thus leading to a higher SR value.

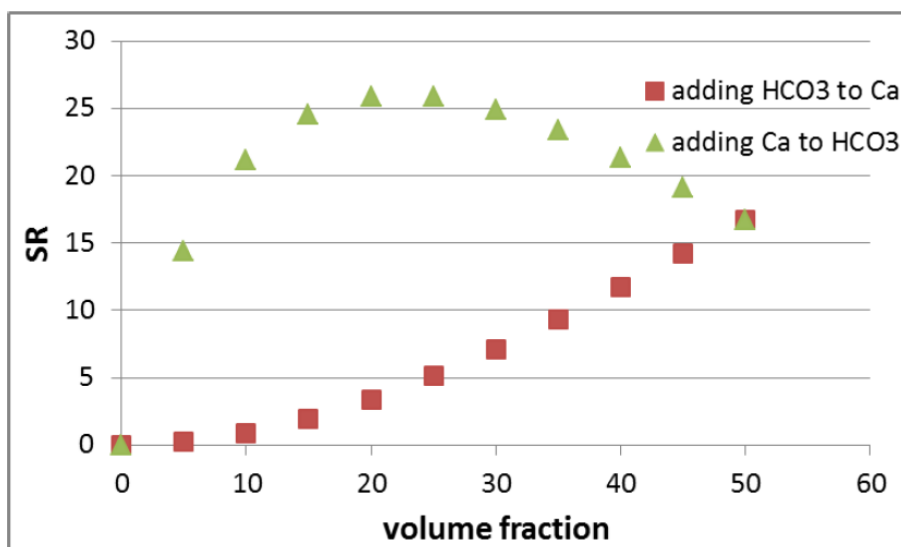


Figure 4. Saturation ratio development of calcium and bicarbonate upon the addition of one to the other. [NaHCO₃] = 0.002 M, [CaCl₂] = 0.05 M.

For the heterogeneous generation of scale on the substrates, it is beneficial that the scale forms slowly, and does not precipitates immediately after adding one of the components. Therefore, adding the NaHCO₃ to the CaCl₂ will produce a slower scale that will preferably adhere to the samples. This was proven by an initial experiment using these two chemicals. However, it was also observed that the concentrations of chemicals can be higher, and further scaling experiments will be conducted using 0.1 M CaCl₂ and 0.2 M NaHCO₃. This difference between experiments and theory is caused by the nature of the NaHCO₃ solution, which changes in time, because of the conversion of HCO₃⁻ to CO₃²⁻.

The surface energies of all samples were measured using a Krüss DSA100 surface tension machine. From the contact angles, the dispersive and polar component of the surface energy can be calculated. The values for these energies are listed in Table 2.

Substrate	Surface modifier	γ_{total} [mN/m]	$\gamma_{dispersive}$ [mN/m]	γ_{polar} [mN/m]
QD	Fluoroacrylate	8.9 ± 0.66	8.5 ± 0.58	0.4 ± 0.08
	Fluorolink F10	14.1 ± 2.2	10.6 ± 1.48	3.5 ± 0.72
	Araldite (2:1)	32.2 ± 2.26	29.3 ± 0.68	2.8 ± 1.58
	Araldite (2:5:1)	29.4 ± 1.49	25.1 ± 0.74	4.2 ± 0.74
	Araldite (2:1.5)	34.6 ± 8.28	29.7 ± 6.43	4.9 ± 1.85
	Sylgard 184	23 ± 0.78	22.1 ± 0.66	0.8 ± 0.12
	TEOS	29.7 ± 1.34	27.7 ± 0.86	2 ± 0.48
	SmartCoat	5.3 ± 0.38	5.2 ± 0.3	0.1 ± 0.08
	TEOS/DTMS (1:1)	21.1 ± 1.86	20 ± 1.58	1 ± 0.28

QD	None	36.7 ± 1.7	29.9 ± 1.0	6.8 ± 0.7
R	None	37.7 ± 1.3	30.6 ± 0.8	7.1 ± 0.6
S	None	32.7 ± 1.4	28.4 ± 1.1	4.4 ± 0.3
Epoxy plate	None	46.9 ± 4.0	38 ± 2.4	8.9 ± 1.7
CaCO ₃	None	39.7	36.0	3.7
Water		52.2	19.9	72.1

Table 2. Surface energies for the substrates and surface modifiers.

The roughness of the substrates is measured using a Sensofar Optical Imaging Profiler. Typical images of the four surfaces are shown in Figure 5 for the three steel panels R, QD and S, and the GFR epoxy substrate. The R-panel is dull finished, and has a more scattered surfaces, whereas QD and S are brushed and polished and show a striped pattern. The epoxy surface appears to be much smoother than the steel plates.

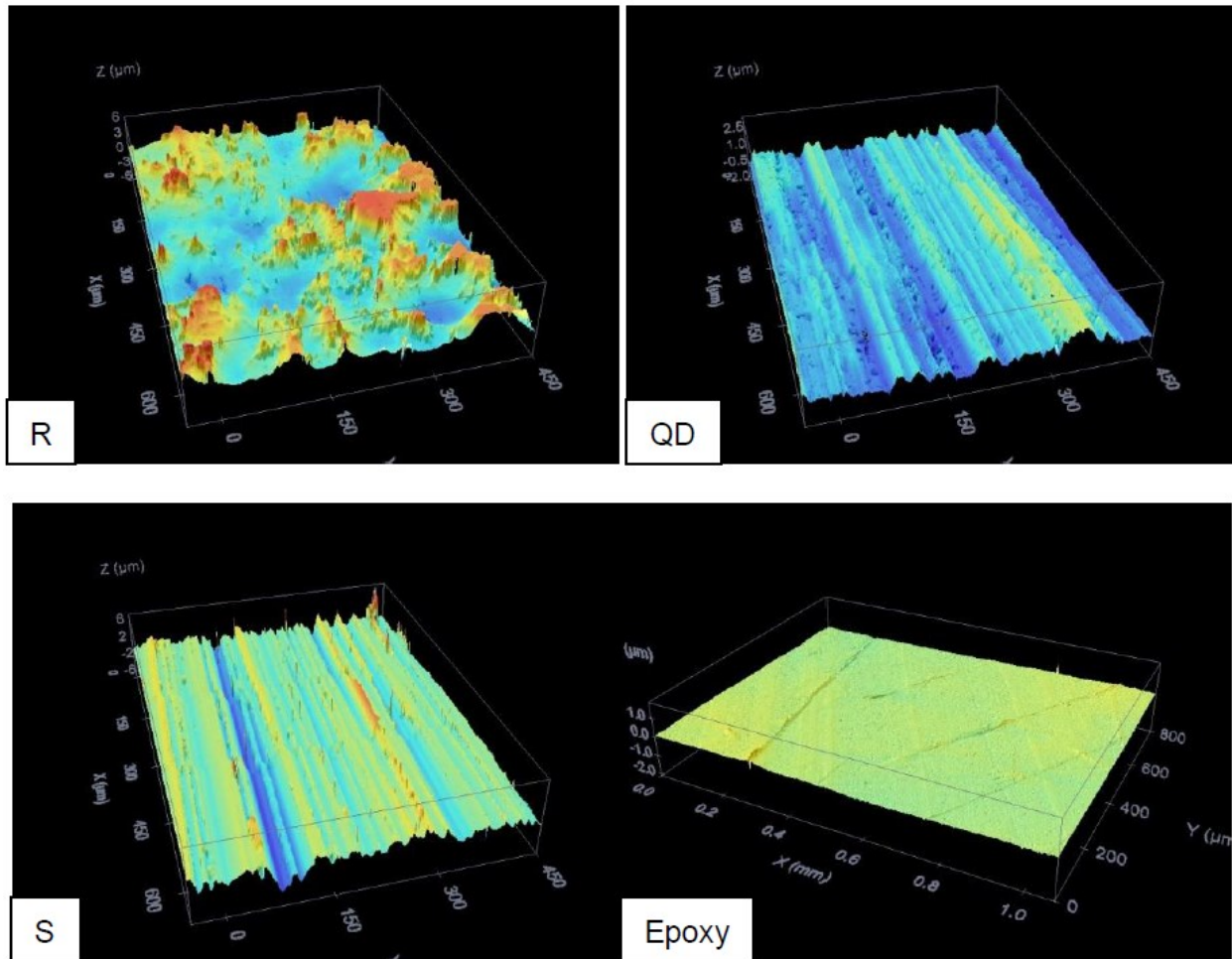


Figure 5. Surface images of the 3 steel substrates panel-R, panel-QD, panel-S and one epoxy substrate.

The values for the roughness parameters are listed in Table 3.

Sample	Finish	Roughness Sa [μm]	Area of peaks, r_1	Area increase, r_2
Q-la Qd	Smooth	0.38	0.81	1.01
Q-lab R	Dull	1.18	0.49	1.07
Q-lab S	Ground	1.02	0.78	1.35
GFR epoxy	No	0.044	0.93	1.01

Table 3. Types and surface properties of steel Q-panel substrates and glass fiber reinforced epoxy. $r_1 = Sh/(Sd+Sh)$ (Sh = mean hill area; Sd = mean dale area); $r_2 = 1 + Sdr$ (=Developed interfacial area ratio).

A set of 30 steel substrates were obtained from the scale experiments. After removing the polymer tubes the scale layers were characterized (Figure 6). The specular light reflection from the surface was measured. The calculated absorbances for the 3 steel panels are listed in tables 4, 5 and 6.

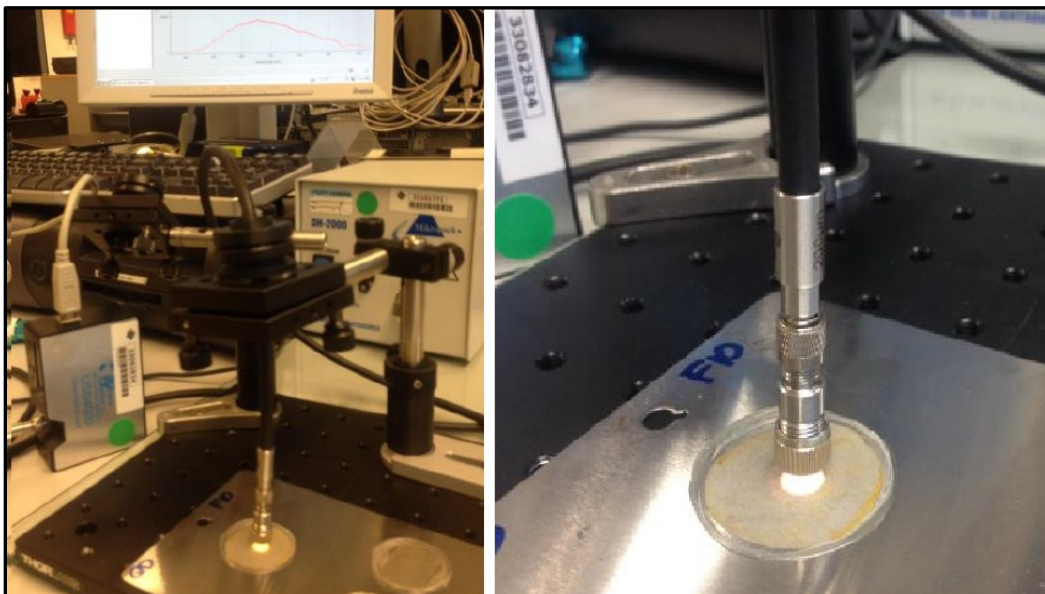


Figure 6. Light reflection measurements on the scaled samples.

Surface modifier	A_Scale	A_Tape	Δ abs
Bare	0.947	0.947	0.000
Sylgard 184	0.269	0.174	0.095
SmartCoat	0.078	0.021	0.057
TEOS/DTMS	0.130	0.097	0.033
TEOS	0.383	0.291	0.092
Fluorolink F10	0.049	0.012	0.037
Fluorocrylate	0.370	0.028	0.343
Araldite (2:1)	0.871	0.812	0.059
Araldite (2:1:5)	0.938	0.935	0.003
Araldite (2.5:1)	0.758	0.737	0.021

Table 4. Q-Panel R: light absorption of the scale layer formed on the treated substrates, before (A_Scale) and after removal by adhesive tape (A_Tape).

Surface modifier	A_Scale	A_Tape	Δ abs
Bare	1.092	1.092	0.000
Sylgard 184	0.471	0.064	0.407
SmartCoat	0.346	0.097	0.249
TEOS/DTMS	0.448	0.453	-0.005
TEOS	0.487	0.502	-0.015
Fluorolink F10	0.348	0.263	0.086
Fluorocrylate	0.368	0.158	0.209
Araldite (2:1)	1.041	0.979	0.063
Araldite (2:1:5)	0.917	0.876	0.041
Araldite (2.5:1)	0.916	0.880	0.036

Table 5. Q-Panel QD: light absorption of the scale layer formed on the treated substrates, before and after removal by adhesive tape.

Surface modifier	A_Scale	A_Tape	Δ_{abs}
Bare	0.553	0.553	0.000
Sylgard 184	0.314	0.290	0.023
SmartCoat	0.087	0.083	0.004
TEOS/DTMS	0.112	0.114	-0.003
TEOS	0.204	0.129	0.074
Fluorolink F10	0.058	0.057	0.001
Fluorocrylate	0.215	0.083	0.133
Araldite (2:1)	0.504	0.437	0.067
Araldite (2:1:5)	0.567	0.497	0.071
Araldite (2.5:1)	0.409	0.333	0.076

Table 6. Q-Panel S: light absorption of the scale layer formed on the treated substrates, before and after removal by adhesive tape

When comparing the bare, untreated steel panels, the S-panel seems to give the least scaling. This is also obvious in the microscope images of the three scaling layers (Figure 7). The amount of crystals (measured as a surface coverage) attached to the S surface is much smaller than the R and QD surfaces. And it appears that the crystal size on the QD panel is smaller.

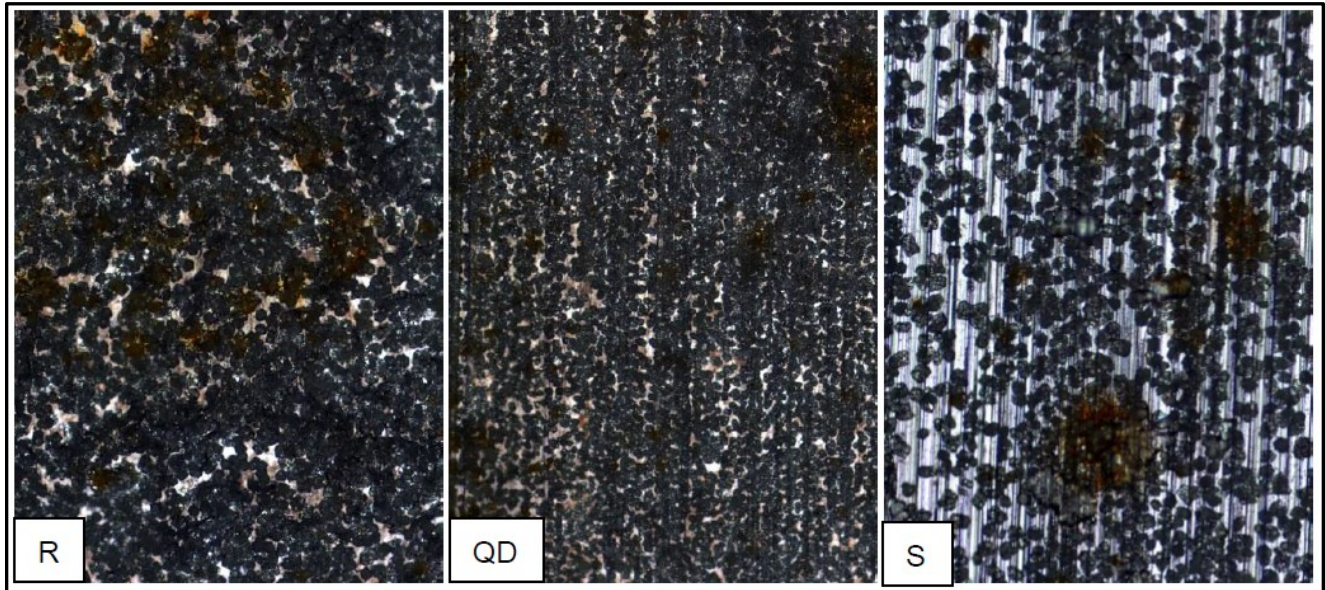


Figure 7. Microscope images of the 3 bare Q-panels, R, QD and S. The calcium carbonate crystals can be seen as the black dots.

Although the surface roughness is almost the same for the Q-panels R and S, the peak density for S is much higher, meaning sharper and more peaks on the surface. So, the roughest surface shows to smallest amount of scaling. The smoothest surface shows the most scaling. An example of the influence of the surface modifier on the scaling tendency is shown in Figure 8. The dark areas are filled with calcium carbonate particles, the light area is reflected light. Three coatings inhibit scale formation, a third (PFTES - Perfluorooctyl triethoxysilane) not.

The conventional way of processing scaling data is by plotting the amount of scaling against the surface energy of the substrate. This is done for the data collected before (A_Scale) and after (A_Tape) removal of all steel substrates using adhesive tape (Figure 9). There is a clear correlation between surface energy and amount of scaling for each Q-Panel. However, each steel panel result in a different amount of scaling. This means that the roughness of the substrate still has a significant influence on the scaling tendency.

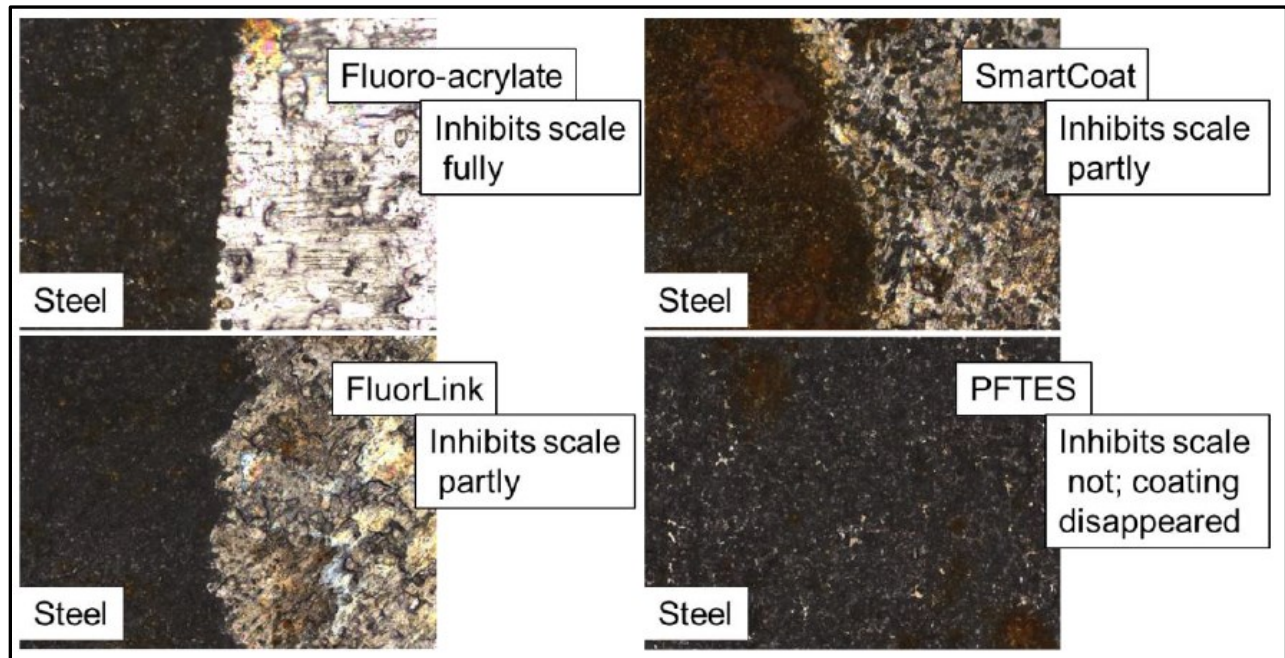


Figure 8. Scaling on coated steel surfaces for 4 different coatings: the PFTES was used in experiments on glass and does not show scale inhibition on steel.

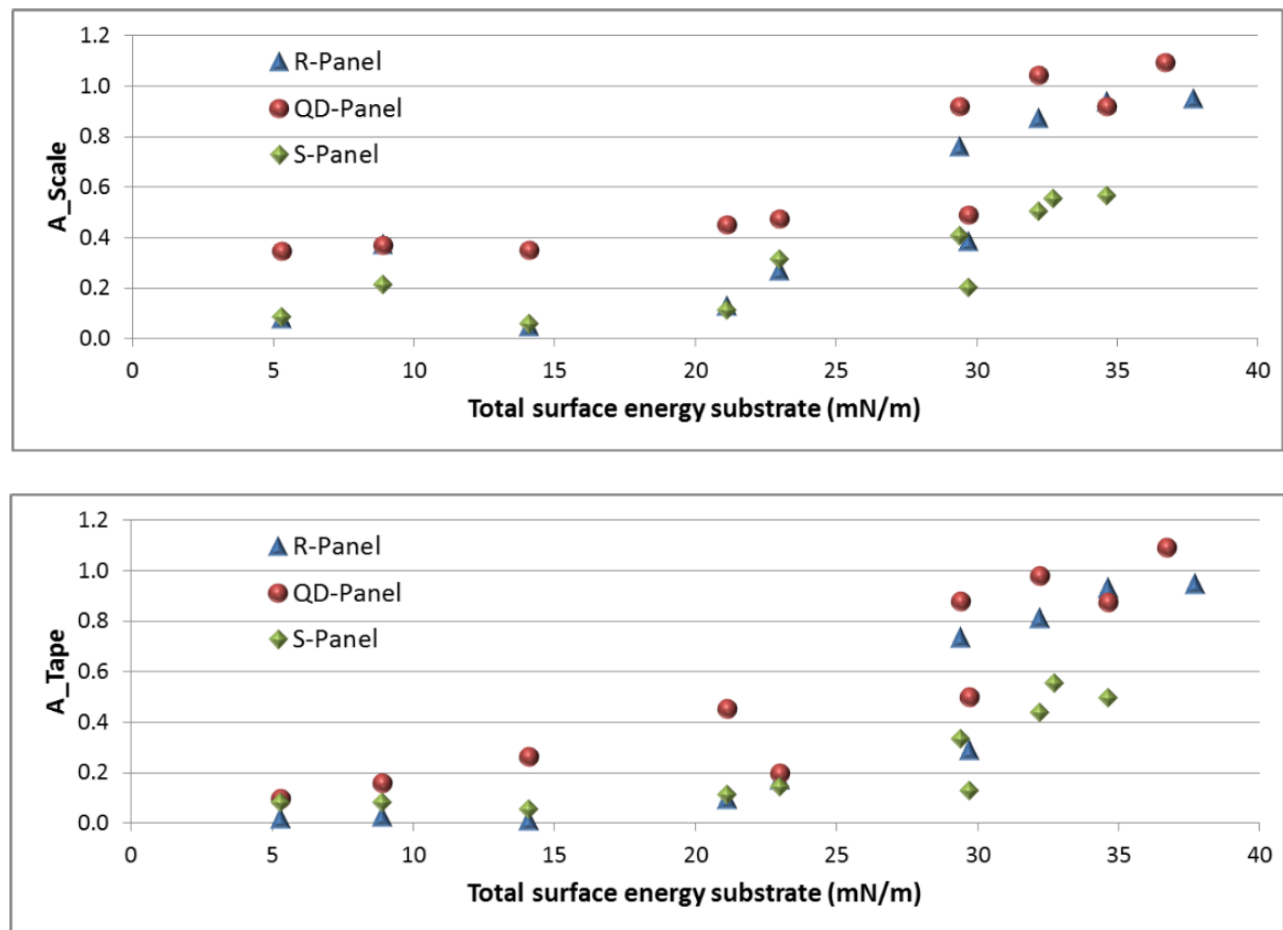


Figure 9. Scaling data (A_{scale} and A_{Tape}) plotted against the total surface energy of the substrates.

The scaling behavior depends on the difference between surface properties of the scaling material and the surface. The work of adhesion can be used to calculate the energy needed to separate a scale crystal from the surface (equation 5). The interfacial energies between the substrate, scale and water can be calculated using the surface energies of the individual components in air. Furthermore, the work of adhesion between scale and a rough surface must be modified because of the differences in contact area:

$$W_{adh} = \gamma_{13} + \gamma_{23} \cdot r_2 - \gamma_{12} \cdot r_1 \quad (9)$$

Where r_2 is the increase in surface area due to the substrate roughness. When the calcium carbonate crystal is released from the surface, water will contact a larger surface because of the roughness. So, $r_2 > 1$. r_1 is the area of contact between the crystals and the surface. This area is smaller than the total area, because the crystals can only adhere to the surface by contact with the peaks of the surface roughness. Consequentially, $r_1 < 1$. We now see that all substrates can be described by a single scaling relation, that depends on the surface energies and some roughness parameters.

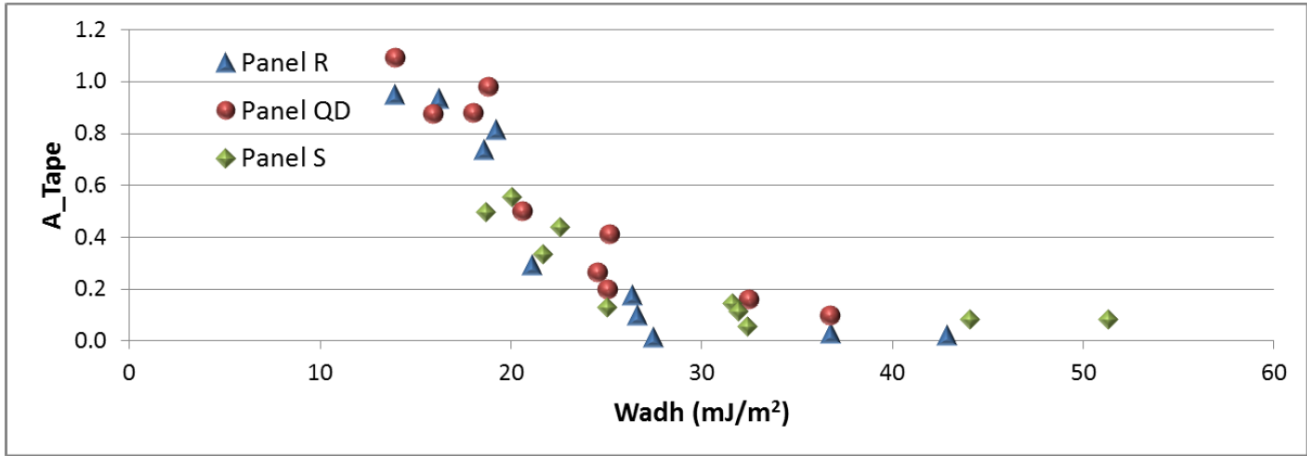


Figure 10. Effective scaling tendency (A_{Tape}) against the work of adhesion of calcium carbonate on the surfaces, corrected for the surface roughness.

The scaling experiments on the glass fiber reinforced epoxy tubing were done in a similar way as the steel samples. Collecting the results it has been found that, surprisingly, the scaling on the Smartcoat coating on GFR epoxy is larger than the same coating on the steel substrates. The scaling on the Fluoroacrylate coating is lower than on the bare epoxy ring, but can be removed easily by the adhesive tape.

The reason that the three epoxy coatings (A2:1, A2.5:1 and A2:1.5) were applied on the steel and on the epoxy ring was the assessment of the influence of scaling on a modified epoxy material. A2:1 is a commercial epoxy, A2.5:1 is made from the same epoxy components (epoxide and amine), but having a larger amount of epoxide groups. A2:1.5 has a higher amount of amine groups, thus changing the surface properties. The surface having the higher amount of epoxide groups (A2.5:1) initially shows more scaling, but can be removed easily. On the other hand, higher amounts of amine (A2:1.5) initially has lower scaling tendency, which cannot all be removed.

When comparing the scaling on the epoxy coatings on the tube and the steel plates, the scaling on the tube is much lower than on the steel plates. This is not caused by the difference in surface roughness, because the smoother surface of the epoxy would result in a higher scaling tendency. Another important difference is the hardness or modulus of the substrates. The coated steel substrates are assumed to have the same modulus as the bare steel, because the thickness of the coatings is very small (~200 nm). If the thickness of the coating increases, than the surface modulus decreases, because it becomes like a pure polymer. This was shown by a scaling test on a thick layer of PDMS, where the light absorption of the scale layer was much lower than that of the thin PDMS layer on the steel.

The adhesion force between scale and substrate is determined by the work of adhesion, and by the surface bulk modulus. The bulk modulus is the most relevant parameter, because the scale crystals are penetrating into the material. The Poisson's ratio has to be taken into account as well. The bulk modulus (K) can be calculated from the tensile modulus (E) by:

$$K = \frac{E}{3 \cdot (1 - \nu^2)} \quad (10)$$

Where ν is the Poisson's ratio. Typical value of the bulk modulus of steel is 160 GPa, and 50 GPa for epoxy. This means that the work of adhesion W_{adh} must be corrected by the square root of the ration between those bulk moduli. This leads to higher work adhesion of the epoxy samples. Finally, the final relation between scaling, surface energy, surface roughness and surface bulk modulus now becomes:

$$A_{Tape} \sim F \sim \frac{K}{W_{adh}} \sim \frac{K}{\gamma_{13} + \gamma_{23} \cdot r_2 - \gamma_{12} \cdot r_1} \quad (11)$$

Where F is the pull-off force (as intended by Chaudhury, 2005).

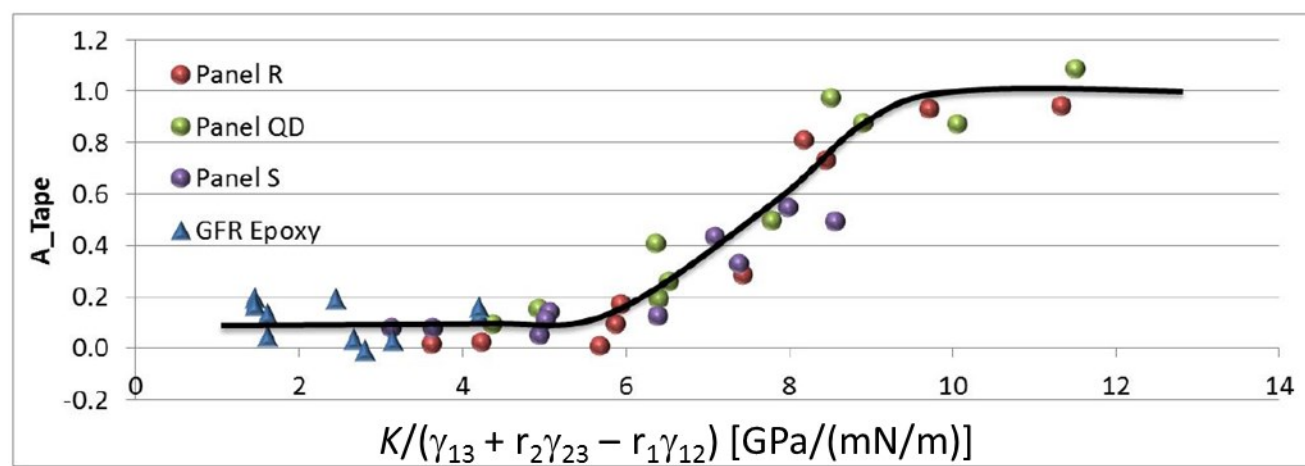


Figure 11. Comparison of the scaling on the three steel substrates and the glass fiber reinforced epoxy substrates.

No significant amount of scale is left on the epoxy tube. This is consistent with the findings on the steel panels.

Analyzing these results, it seems to be a transition area between low and high amounts of scale development. When the value $\frac{K}{\gamma_{13} + \gamma_{23} \cdot r_2 - \gamma_{12} \cdot r_1}$ is smaller than 6 GPa/(mN/m), low amounts of scale will occur. When this value becomes higher than 6 GPa/(mN/m), scale starts to develop until a value of 10 GPa/(mN/m), where the whole surface is covered with a scale layer. Although this relation must be furtherly validated for more substrate-scale systems, it is a very promising approach to be used to assess the scaling tendency of various types of wellbore systems.

4. CONCLUSIONS

In our study we show that the amount of scaling that is deposited on a substrate depends on three parameters: surface energy of the casing, roughness of the surface and the bulk modulus of the surface. These parameters were used for the development of a single parameter that can describe the scaling tendency of a surface. A more long term solution for scaling prevention is the implementation of a casing material that is intrinsically better resistant against scaling. A new class of pipes that may show intrinsically improved scaling performances is glass fiber reinforced composites. The inner surface of the pipes consist of the polymer matrix of epoxy or polyethylene and will have a different surface energy than steel pipes. Several sets of experiments were done on steel and polymer matrix casings under static scaling conditions, where a mixture of CaCl_2 and NaHCO_3 was placed on top of the surface treated substrates for certain periods of time. The scale that formed was a combination of heterogeneous nucleated on the surface and homogeneous nucleated in the bulk solution. The latter scale was removed by rinsing the samples and an adhesive tape after drying to only assess the scale that was grown on the surface. Moreover, we have shown that the measurement of the light reflection from the scaled surface is a good way of assessing the amount of scaling. With the results collected in this study, it is possible: predict the scaling tendency under specific conditions, measure the scale to validate the predictions and assist the development of material for pipelines to lower scaling risks.

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