Quantitative comparison of anaerobic pitting patterns and damage risks by chloride versus *Desulfovibrio vulgaris* using a fast pitting-characterization method

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Abstract

Anaerobic carbon steel corrosion induced by chloride and a sulfate reducing bacterium (SRB) *Desulfovibrio vulgaris* was compared using a fast pitting-characterization method based on Infinite Focus Microscopy. This method was found to be significantly less labor-intensive and more reproducible for determination of maximum and average pit depths and pitted area percentage than manual pit identification and measurement. Graphic diagrams were developed with these parameters to show pitting patterns and compare damage risks. Results showed that this SRB was more damaging than chloride by forming deep pit clusters with larger maximum pit depths. Pit geometry and size were also compared for the two corrosion causes. The fast pitting-characterization method was validated to work well for corrosion with different pitting patterns and pit geometries induced by the chloride and *D. vulgaris* systems.

Keywords: carbon steel; pitting corrosion; microbiologically influenced corrosion; infinite focus microscope; sulfate reducing bacteria; chloride; surface roughness.

1. Introduction

Anaerobic condition exists even in bulk aerobic water, especially in stagnant water where convective oxygen supply is limited (Richards et al., 1965). Carbon steel is widely used in water environments, where anaerobic condition often occurs (Lee et al., 2004). Sulfate reducing bacteria (SRB) are notorious in inducing pitting corrosion under anaerobic conditions (Chen et al., 2015 ; Dinh et al., 2004; Enning and Garrelfs, 2014; Enning et al., 2012; Javaherdashti, 2011). Pitting corrosion may cause disastrous failures such as rupture and leakage (Frankel, 1998; McCafferty, 2010). Chloride is another well-known cause of pitting (Frankel, 1998; Marcus, 2011). Steel pitting has been well studied in aerobic chloride solutions or sterilized seawater (Alvarez and Galvele, 1984; Cáceres et al., 2009; Melchers and Jeffrey, 2014). On the other hand, studies on chloride induced pitting under anaerobic conditions have been more limited. Reported corrosion rates of carbon steel in anaerobic chloride solutions were low (Duan et al., 2008; Peña et al., 2008; Smart et al., 2006). One report included the pitting of carbon steel in sterilized anaerobic seawater but showed only 1 microscopic image without quantitative characterization (Xu et al., 1999). Surface roughness also affects the pitting outcome. It was observed that rougher surfaces caused more but shallower micro pits, while smoother surfaces induced fewer but deeper pits (Chen et al., 2014; Melchers, 2004; Szklarska-Smialowska, 1986). Pitting corrosion resulting from different causes may have different pitting patterns and pit geometries and, more importantly, may elicit different levels of failure risk. Detailed, quantitative comparisons of pitting corrosion from

different causes are important to the fundamental understanding and the corrosion failure evaluation and prediction.

Literature reports on quantitative characterization of pitting corrosion are rare. Many reported only the results of weight loss measurement or microscopic observation of the pitted surfaces (Ilhan-Sungur et al., 2007; Rao et al., 2005; Xu et al., 1999). However, the few microscale images shown were not suitable for representing the pitting extents of large surfaces because pit distribution could be highly localized, and weight loss results often did not represent the pitting damages (Chen et al., 2014; Xu et al., 1999). ASTM G46-94 (ASTM, 2005b), a standard guide for examination and evaluation of pitting corrosion, specifies several pitting parameters that need to be determined. Maximum pit depth is the most critical parameter, since it is related with the risk of material failure (Nessim, 2000; Velázquez et al., 2014). Pit density, average pit width and depth are also important, according to the standard rating chart for pits (ASTM, 2005b). However, gathering these data by microscopic methods can be labor-intensive and time-consuming, especially for large surfaces with numerous pits. For example, Infinite Focus Microscopy (IFM) is widely used by corrosion researchers (Chen et al., 2014; Farelas et al., 2012; Jiang et al., 2012; Winkler et al., 2010; Xu and Gu, 2014; Xu et al., 2013), but quantitative characterization of a pitted surface still requires manual identification and individual measurement of all the pits on the surface. In addition, the average pit depths or widths obtained typically have large standard deviations because the surfaces may contain pits with widely varying depths and widths. On surfaces with highly localized corrosion, the standard deviations can be even larger than the average values. Drawing statistically meaningful conclusions from these data can be challenging.

Recently, Chen and Ju (Chen and Ju, 2015) developed correlations that allowed fast determination of maximum and average pit depths and the percentage of pitted area from the standard 3D surface parameters (ISO, 1996; Stout et al., 1993) obtainable with IFM. In addition, a four-phase diagram with the average pit depth as y-axis and the pitted area percentage as x-axis was shown to be able to categorize different pitting patterns and to indicate pitting extents. This previous work was based on the results of carbon steel pitting caused by *D. vulgaris*.

In this study the reported correlations by the fast pitting-characterization method were evaluated for accuracy in determining the pitting parameters caused by both *D. vulgaris* and chloride on carbon steel coupons with different surface roughness. The 4-phase diagram was adopted for comparing the pitting patterns caused by *D. vulgaris* and chloride. A new diagram, with maximum pit depth as the y-axis and pit volume loss (V_w) as the x-axis, was proposed in this study to assess the pitting-associated failure risk. To complete the comparison of pitting by chloride and *D. vulgaris*, the pit width/depth aspect ratio (AR) vs. area-box (AB) diagrams proposed by Codaro et al. (Codaro et al., 2002) were also generated for pit geometry comparison. The area-box was defined as

the cross-sectional area of the pit over the area of the smallest rectangular box that enclosed the pit. Preparation of these AR vs. AB diagrams still required extensive labor to measure the pit depth and cross-sectional area of each individual pit.

2. Materials and Methods

2.1. Carbon steel coupon preparation

Rectangular (25 × 11 × 0.3 mm) carbon steel (UNS G10100) coupons were used. Maximum contents (in mass %) of non-iron elements in the carbon steel were 0.60% manganese, 0.13% carbon, 0.030% phosphorus and 0.035% sulfur. One side of the coupons was not polished. The other side was polished with increasingly higher grit SiC sand papers, i.e., 240/P280, 600/P1200, 800/P1500, and 1200/P2500 (8" diameter, Carbimet 2, Buehler Company), using a polishing machine (Model DAP-7, Struers, Inc.) at a speed of 200 rpm. Deionized water was added to rinse and cool the coupons. Coupons were then cleaned by sequential sonication in acetone and ethanol. To avoid collision and rubbing between the coupons during sonication, only 1 layer of non-overlapping coupons were placed in a large beaker (13 cm in diameter). After sonication cleaning in acetone and then ethanol, we examined and characterized the coupons prior to corrosion test using IFM (Alicona imaging GmbH, Bartlett, IL) to ensure the coupons after cleaning were still free of pits or defects. For sterilization, coupons were soaked in pure ethanol for 2 days at room temperature (with sonication during 0 - 2 h and 46 – 48 h to remove gas bubbles on coupon surfaces). Coupons were then aseptically dried inside a laminar flow hood with filter-sterilized air (Environmental air control Inc.). More detailed description about the initial 3D surface parameters on the polished and unpolished surfaces is available elsewhere (Chen et al., 2014).

2.2. Carbon steel coupon characterization

Prior to the examination by IFM, coupons were cleaned for 40 min with Clarke's solution following the ASTM G1-03 standard chemical cleaning procedure for iron and steel (C.3.1 in Table A1.1) (ASTM, 2003). Surface pit morphology, maximum pit depth, pit density, percentage of pitted area, average pit depth, and statistical roughness information were obtained from the 3-dimensional (3D) IFM images. The lateral resolution of the 3D IFM image was 0.4 μm and the vertical resolution was 0.2 μm. Each scan provided the following images and information required for obtaining pitting parameters in this study: (1) a 2D top view image and a side profile view for pit depth measurement; (2) a 3D image (compiled from multiple focused 2D images) with top, side and angle views for pit density and pitted area percentages measurements; and (3) the 3D surface parameters. To obtain valid 3D surface parameters, proper pre-processing of the 3D images was very important, including reference plane adjusting, form removal and roughness filtering. The reference plane was adjusted using the built-in Robust

method (Stout et al., 1993). To eliminate disturbance of sample shape (form), 3D surface filtering was carried out to extract the “roughness” profile from the “primary” profile. The “waviness” profile, which reveals the more gradual surface change, was filtered out. The cutout wavelength L_c was selected according to color preview of surface filtering. The proper L_c is the highest wavelength, at which the entire surface appears in the same color except for the areas with pits. Edge and areas with defects (other than pitting) were excluded from scanning. More details are available elsewhere (Chen and Ju, 2015).

To locate the deepest pit, the entire coupon surface was skimmed by IFM 2D view to identify the possible candidates. All deep pits were measured and compared to determine the maximum pit depth. Average pit depth was calculated from all manually measured depths for at least 50% of the pits. Pitted area percentage was obtained by analyzing the IFM 3D top-view images using Image J (National Institutes of Health, Bethesda, MD). These experimentally measured maximum and average pit depths and pitted area percentage were later compared with the values calculated from the IFM 3D surface parameters using the correlations described in Section 3.1. Cross-sectional areas of pits, required for generating the AR vs. AB diagram as described in more detail in Section 4.6, were determined using AutoCAD 2013 (Autodesk, San Rafael, CA). Weight loss rate was calculated based on the weight loss measurements according to the ASTM standard method (ASTM, 2005a). All coupons were weighed before the corrosion study and weighed again after being removed from the test systems and cleaned (ASTM, 2003).

2.3. Corrosion experiments

2.3.1 Carbon steel incubated with anaerobic *D. vulgaris* culture and abiotic medium

Desulfovibrio vulgaris ATCC 7757 was used in this study. The *D. vulgaris* seed culture was grown with Postgate medium C in serum bottles (Supelco, Milwaukee, WI). All cultivation procedures were conducted under anaerobic and sterile conditions (Chen et al., 2013). The medium was sealed in a serum bottle with butyl rubber stopper, which was crimped with aluminum seal. N_2 gas was bubbled through the medium while the bottle was heated to 100 °C for 20 min. The serum bottle was then autoclaved at 121 °C for 20 min. A cysteine stock solution (oxygen scavenger), similarly treated with N_2 and sterilized, was added to the medium to a final cysteine concentration of 2 mg l⁻¹. Stock *D. vulgaris* culture with 20% glycerol was preserved in a freezer at -70 °C. The stock culture was thawed and inoculated at 5% (by volume) to the medium. After incubating at 25 °C for 1 day, the culture would reach the early stationary phase with a cell concentration of approximately 1.4×10^9 cells ml⁻¹. These cells were used as the inoculum (at 5% v/v) for the corrosion reactors with submerged carbon steel coupons. Optical density at 600 nm (OD₆₀₀) was measured using a UV–Vis spectrophotometer (Model 1601, Shimadzu Corp., Canby, OR).

The corrosion experiments were done in six reactors, each containing 4 carbon steel coupons immersed in either the Postgate medium C inoculated with the *D. vulgaris* culture or a sterile Postgate medium C (without pyruvate or yeast extract to mimic the composition in the SRB system where these compounds would be depleted in the first 2 days of growth). Systems were routinely checked for contamination by confocal laser scanning microscopy (Carl Zeiss AG, Jena, Germany) and optical microscopy (Olympus America Inc., Center Valley, PA). 600 mL glass Griffin beakers with the top section containing the pour spout cut out and closed with rubber stoppers (size 14, Cole-Parmer, Vernon Hills, IL) were used as incubation vessels. Stainless steel hooks were inserted into the rubber stopper and plastic tie wraps were used to tie the coupons to the hooks through a small hole at one end of the coupon. The hooks were maintained above the liquid throughout the experiment. All 4 coupons from one reactor were taken for IFM characterization at one sampling time, on Day 3 or 21 or 43. The concentrations of pyruvate and other metabolic products were measured with a high-performance liquid chromatography (HPLC) system (LC-10A, Shimadzu Corp., Columbia, MD) equipped with a Supelcogel H column (Sigma-Aldrich Corp., St. Louis, MO) and a UV-Vis detector (SPD-10A) (Chen et al., 2015). The medium used in this set of SRB-inoculated experiments had 19.2 mM chloride, much lower than that in sea water (approximately 600 mM). More details about *D. vulgaris* cell metabolism are available elsewhere (Chen et al., 2015).

2.3.2. Carbon steel incubated with 3.5% NaCl solution

This second set of corrosion experiments were performed with the carbon steel exposed to 3.5% NaCl solution in deionized (DI) water, to mimic seawater, in stoppered serum vials under sterile and anaerobic condition. Two serum vials, each holding 2 carbon steel coupons, were used. The carbon steel coupons were hung on Teflon hook that was anchored on the rubber stopper and were completely submerged in the 3.5% NaCl solution. The serum vials and contents were purged with nitrogen gas for 30 min before the corrosion experiments. The serum vials and the NaCl solution were sterilized by autoclaving at 121 °C for 30 min. The pitting corrosion on these coupons was examined on both polished and unpolished sides at two exposure times, i.e., 3 and 21 days.

3. Pitting Characterization Methods

In this study the pitting corrosion was characterized with large numbers of IFM scans. For the *D. vulgaris* systems, 124 sets of images, each with the equipment (IFM) default scanning area of 0.85 mm², were recorded for each surface. These images, including both pitted and non-pitted areas, covered nearly 40% of the entire surface area, which was 275 mm² for each side of coupon. So, 3 coupons (6 sides) were scanned at each exposure time, totaling 744 sets of images. On the other hand, in the 3.5% NaCl systems,

since the coupons were found to be pitted in limited areas, only the areas having at least one micro pit with depth larger than 2 μm were located and scanned. Accordingly, at Day 3, 52 sets of images were scanned on the coupon, 26 each on the polished and unpolished sides, while at Day 21, 136 sets of images were scanned, 67 sets on the polished side and 69 sets on the unpolished side.

3.1. IFM obtainable surface parameters and correlations to maximum and average pit depths and percentage of pitted area

Based on the earlier results of carbon steel pitting corrosion by the SRB *D. vulgaris*, correlations were previously established between three IFM-obtainable 3D surface parameter groups and the maximum pit depth, average pit depth and pitted area percentage determined from individually identified and measured pits (Chen and Ju, 2015). The IFM parameters used were (DIN, 1990; ISO, 1997; Stout et al., 1993)

S_{pk} : mean height of the peaks above the core material (μm),

S_k : height of the core material or kernel (μm),

S_v : maximum valley depth (μm),

S_{vk} : mean depth of the valleys below the core material (μm),

V_{vv} : valley void volume of the surface (ml m^{-2}), and

S_{dr} : developed interfacial area ratio (%),

$= (\text{actual surface area} - \text{projected surface area})/(\text{projected surface area}) \times 100$.

Surface was divided into three parts—peak, core and valley. S_{pk} was the mean height of peak material, while S_k represents surface roughness. Since valleys correspond to pits, the valley parameters (S_v , S_{vk} and V_{vv}) correlate with pitting extent.

The correlations established were given below:

$$\text{Maximum pit depth } (\mu\text{m}) = 0.96 \times (S_v + S_k) \quad \text{Eq. 1}$$

$$\text{Average pit depth } (\mu\text{m}) = 1.17 \times (S_{dr}/V_{vv}) + 6.23 \quad \text{Eq. 2}$$

$$\text{Pitted area } (\%) = 6.62 \times (S_{vk} \cdot V_{vv}/S_{dr}) \quad \text{Eq. 3}$$

3.2. Pitting pattern diagram (four-phase diagram)

The previously developed four-phase diagram (Chen and Ju, 2015) was developed using around 700 sets of IFM 3D images of pits. The y axis of this diagram was the average pit depth, estimated from the S_{dr}/V_{vv} value using Eq. 2, and the x axis was the percentage of pitted area, estimated from the $S_{vk} \cdot V_{vv}/S_{dr}$ value using Eq. 3. Pits in each 3D image were observed and the depths were measured manually. The manually observed and measured pitting pattern was compared with the pitting pattern indicated by the 4-phase diagram for verifying the adequacy of this diagram. According to this diagram, the pitting corrosion data could be divided into 4 phases that represent 4

different pitting patterns (Chen and Ju, 2015) Phase I – few or no micro pits (pitted area percentage < 1.7 %, average pit depth < 10 μm), Phase II – many micro pits or large shallow pits (pitted area percentage > 2.2 %, average pit depth < 10 μm), Phase III – few narrow deep pits (pitted area percentage < 1.7 %, average pit depth > 14 μm), and Phase IV – deep pit cluster with or without micro pits (pitted area percentage > 2.2 %, average pit depth > 14 μm). In this diagram, deep pits are defined as those with depths of at least 15 μm and deep pit clusters are defined as to have at least 3 deep pits in one scanned area (0.85 cm^2).

3.3. Failure risk diagram

In addition to the 4-phase pitting pattern diagram, a new diagram was developed in the current work to better differentiate the pitting-associated failure risk. The pit with maximum depth was considered the most vulnerable site for failure (ASTM, 2005b; Nessim, 2000; Velázquez et al., 2014). Therefore, the failure risk diagram uses the maximum pit depth ($S_v + S_k$, μm) as y axis. The pit volume loss (V_w , ml m^{-2}) was chosen as x axis because it represents the combined effects of average pit depth and pitted area percentage. For surfaces with similar maximum pit depths, the surfaces with larger V_w were assumed to have higher failure risk. Together, the 4-phase pitting pattern diagram and the new failure risk diagram were used to compare and rate the pitting corrosion occurring under different conditions evaluated in this study.

4. Results and Discussion

4.1. Comparison of weight loss rate by chloride and *D. vulgaris* under anaerobic condition

In an earlier study, weight loss of carbon steel was found to be mild under the anaerobic condition, no matter if the metal was incubated with the *D. vulgaris* cells or in the abiotic medium with a low chloride concentration (Chen et al., 2014). The same was observed in this study as shown by the low weight loss rates. For both the SRB and NaCl (3.5%) systems, the rates were higher during the first 3 days ($91.2 \pm 16.3 \mu\text{m y}^{-1}$ for *D. vulgaris* and $29.5 \pm 13.5 \mu\text{m y}^{-1}$ for NaCl) than those measured at Day 21 ($10.0 \pm 0.8 \mu\text{m y}^{-1}$ for the SRB and $21.2 \pm 6.2 \mu\text{m y}^{-1}$ for NaCl). The corrosion induced by *D. vulgaris* and chloride was presumably caused by different mechanisms. For the *D. vulgaris* system, the biofilm thickness and coverage were significantly higher at Day 21 than at Day 3; the thicker biofilm probably protected the metal surface and lowered the weight loss rate (Chen et al., 2015). In the NaCl system, the corrosion rates at Day 3 and Day 21 did not differ significantly ($p = 0.53$). Nevertheless, these observed weight loss rates were low; all were within the range of 0 – 100 $\mu\text{m y}^{-1}$, generally considered as excellent in relative resistance to uniform corrosion (McCafferty, 2010). The corrosion rate of $21.2 \pm 6.2 \mu\text{m y}^{-1}$ found in this study for the chloride system under the anaerobic condition tested was

far less aggressive than the rate, e.g., $508 \mu\text{m y}^{-1}$, reported for the similar chloride systems under aerobic conditions (Acharya and Upadhyay, 2004). It is concluded that under the anaerobic condition, neither the *D. vulgaris* cells nor the chloride ions caused significant weight loss on carbon steel.

4.2. Characterization of coupons before *D. vulgaris* exposure

As shown in Table 1, polished surface has much lower average S_{pk} and standard deviation than the unpolished surface, while S_k and S_{vk} were similar. This indicates that the peak material was polished out during polishing process. S_{vk} values, the average valley depth, were very small on both polished ($0.47 \pm 0.06 \mu\text{m}$) and unpolished sides ($0.42 \pm 0.10 \mu\text{m}$), which suggested that no pit was present on coupons before *D. vulgaris* exposure. After 21d *D. vulgaris* exposure, when severe pitting was induced, both average values and standard deviations of S_{vk} increased significantly ($1.88 \pm 1.65 \mu\text{m}$ on the unpolished side) than coupons before *D. vulgaris* exposure. 3D surface parameters measure the average roughness including pitted and unpitted areas. Due to this average nature, pit depth information was not intuitively clear.

4.3. Characterization of starvation condition

Cell concentration (measured as optical density at 600 nm) and pyruvate concentration profiles were followed in a serum vial in the absence of carbon steel coupons. As shown in Figure 1 (a), during the first day, the carbon source pyruvate was consumed, while *D. vulgaris* cells actively grew with OD_{600} increase from 0.03 to 0.66. After pyruvate depletion, cells experienced death phase with OD_{600} dropping from 0.66 to 0.28. This indicated that cells were under organic electron donor starvation; otherwise cells would have continued growing or maintained a relatively stable concentration. Yeast extract, another organic nutrient in the fresh medium, was included as a source of organic nitrogen and growth factors to promote cell growth. It did not prevent cells from dying after pyruvate exhaustion.

In the corrosion study, *D. vulgaris* was incubated in the presence of carbon steel coupons. As shown in Figure 1 (b), pyruvate was completely consumed during the first 2 days. Similar to the observations in the coupon-free system, cells in liquid phase of the corrosion-study reactors experienced starvation of organic electron donor after complete depletion of pyruvate.

4.4. Comparison of pitting characteristics induced by chloride and *D. vulgaris* under anaerobic condition

Although the weight loss rates were low in both the *D. vulgaris* and chloride systems, pitting was clearly observed in these systems. For carbon steel that had been incubated with 3.5% NaCl for 21 days, pitting was seen along some scratch lines presumably generated during polishing (Figure 1 (c)). On the other hand, random

clusters of deep pits were found on the carbon steel incubated with *D. vulgaris* (Figure 1 (d)). Chloride and *D. vulgaris* induced different pitting characteristics presumably because they involved different corrosion mechanisms. Chloride ion is considered as an aggressive chemical that can breakdown the passive corrosion product film (Cruz et al., 1998; Frankel, 1998; Loto, 2013). Defects such as polishing lines or scratches influence the protective property of passive film (Szklańska-Smiałowska, 1986) and the areas near these defects may be at higher risk for chloride ion penetration. This may be responsible for the observed pitting along the polishing lines in the NaCl systems. For *D. vulgaris* systems, pyruvate, the organic electron donor in the initial medium, was completely consumed in the first 2 days (Figure 1 (b)). The HPLC analysis results showed no consumption of organic compounds in the liquid broth afterwards, indicating that the cells were starved of exogenous organic substrates after the initial growth. The proposed mechanism of SRB-induced corrosion was that the organics-starving cells attached to the steel surface could derive energy for their survival by coupling iron oxidation with sulfate reduction, which caused the pitting (Chen et al., 2015 ; Sherar et al., 2011; Xu and Gu, 2014). Because pitting corrosion induced by *D. vulgaris* was associated with biofilm attachment (Chen et al., 2015), the resultant pits were more randomly dispersed on the carbon steel surface (Figure 1 (d)). According to Figure 1 (c) and (d), both average pit depth and pit density seemed to be higher in the *D. vulgaris* system than in the NaCl solution. However, a few SEM images from some randomly picked small areas are not enough to conclude on the different extents of pitting. Information gathered from an entire surface would be more meaningful, as described in the following sections.

Coupons removed after 43 days from the abiotic control were covered with corrosion products. Entire surfaces of these coupons, after cleaning, were examined with IFM. There was no clear pitting attack. The representative surface morphology is shown in Figure 1 (e) for a coupon sample taken after 43 days.

4.5. ASTM standard method specified pitting parameters in chloride versus *D. vulgaris* systems on carbon steel of different surface roughness

ASTM standard method (ASTM, 2005b) specifies several characteristic parameters to measure for quantifying pitting corrosion. These parameters were measured and compared in Table 2 for the anaerobic carbon steel corrosion by the *D. vulgaris* cells versus the 3.5% NaCl. When focused only on pit density and maximum pit depth, the following conclusions can be clearly drawn from the results summarized in Table 2: (1) Compared to the 3.5% NaCl, *D. vulgaris* induced deeper pitting on carbon steel, giving consistently higher pit density and maximum pit depth for the same exposure time and surface roughness. For example, the *D. vulgaris* system caused a pit density of 4.78×10^5 pits m^{-2} and a maximum pit depth of 46 μm at 21 days on the polished surface, whereas the NaCl system caused only a pit density of 3.44×10^4 pits m^{-2} and a maximum pit depth of 32 μm . (2) In both systems the coupons incubated for 21

days showed more severe pitting than the coupons incubated for only 3 days. For example, on the unpolished carbon steel surface exposed to the NaCl solution, the pit density (2.72×10^5 pits m^{-2}) and maximum pit depth (24 μm) at 21 days were higher than those (1.98×10^5 pits m^{-2} , 14 μm) at 3 days. (3) Unpolished surfaces have consistently higher pit density than their polished counterparts. For example, after 21 days in the *D. vulgaris* system, the pit density on the unpolished surface (3.00×10^7 pits m^{-2}) was higher than that on the polished side (4.78×10^5 pits m^{-2}).

On the other hand, neither average pit depth nor average pit width showed any clear trends or differences because of the large standard deviations associated (Table 2). For example, the polished carbon steel surface in the *D. vulgaris* system had an average pit depth of 9 ± 7 μm and an average pit width of 46 ± 32 μm at Day 3, which were not statistically different from the average pit depth of 12 ± 9 μm and average pit width of 55 ± 17 μm at Day 21. These uncertainties cause incomplete characterization of pitted surfaces, if relying on just maximum pit depth and pit density. For example, a surface with many pits of depths similar to the maximum pit depth is clearly different from a surface with only one deep pit at the maximum depth and many micro pits. Besides the issue of large standard deviations for average pit depth and width, determining these parameters from measurements of individually identified pits required excessive time and effort. A faster and improved method was needed for quantitative characterization of pitted surfaces.

4.6. AR vs. AB diagram for pit geometry classification

Pitting corrosion of the systems with *D. vulgaris* or 3.5% NaCl was evaluated using the AR vs. AB diagram proposed by Codaro et al. (Codaro et al., 2002) as shown in Figure 2 and Table 3. For the AR vs. AB diagram, the y-axis AR is the width/depth aspect ratio and the x-axis is the area-box (AB) parameter defined as the ratio between pit area and the area of the smallest rectangle (the box) that encloses the pit. Codaro et al. (Codaro et al., 2002) classified pit geometry, i.e., conical, cylindrical, and spherical or hemispherical, according to their 2D side-view shapes, i.e., triangle, rectangle, and circle or semicircle. Each shape family contains around 20 test pictures with fixed width but different AR (0-15). AR vs. AB diagram was calibrated with these test pictures for the three shape families. It was shown that all the triangles (conical pits) have AB values of about 0.5, all the circles or semi-circles (spherical or hemispherical pits) have AB values of about $\pi/4$, and all the rectangles (cylindrical pits) have AB values of about 1. Other than these well-defined pit geometries, some pits had irregular shapes (with $\text{AB} < 0.5$) or were during shape transition ($0.54 < \text{AB} < 0.72$ or $0.86 < \text{AB} < 1$). Accordingly, the diagram was divided into 7 regions (I to VII, as labeled in Figure 2), each corresponding to a specific pit shape: (I) irregular pits, $\text{AB} < 0.5$; (II) conical pits, $0.5 < \text{AB} < 0.54$; (III) shape transition A, $0.54 < \text{AB} < 0.72$; (IV) hemispherical pits, $0.72 < \text{AB} < 0.86$; (V) shape transition B, $0.86 < \text{AB} < 1$; (VI) cylindrical pits, $\text{AB} = 1$; and (VII) spherical pits, $0.72 < \text{AB}$

< 0.86 and $1 < AR < 2$. Figure 2 (c) showed the representative geometries for the 6 regions observed in the *D. vulgaris* systems. The shape transition phases A and B refer to the pits that fell into the range between the two nearby phases. For example, as shown in Figure 2 (c), shape transition B (phase V) showed a pit with a morphology combining hemispherical (phase IV) and cylindrical pit shapes (VI). As shown in Figure 2, most scanned areas in this study fell in Regions I, II and III, particularly concentrated in or near Region II. Thus, the NaCl and *D. vulgaris* systems induced mostly conical or nearly conical pits.

The percentages of pits in different regions (shapes) for the pits shown in Figure 2 are summarized in Table 3. Between the *D. vulgaris* and 3.5% NaCl systems, the main difference of pit geometry was that consistently higher percentages of cylindrical pits were observed in the *D. vulgaris* systems than for the surfaces exposed to the NaCl systems under the same experimental conditions. For example, on the unpolished surfaces observed at 21 days, the percentage of cylindrical pits in the *D. vulgaris* system was 20.8%, while it was only 0.8% in the NaCl system. Surface roughness also had a significant effect: cylindrical pits appeared at higher percentages on the polished side than on the unpolished side in both NaCl and *D. vulgaris* systems. For example, in the *D. vulgaris* system the percentage of cylindrical pits on the polished side (13.3%) was much higher than that on the unpolished side (3.7%).

4.7. Pitting pattern and failure risk diagrams

4.7.1. Correlations for maximum pit depth, average pit depth, and pitted area percentage

As described earlier, linear correlations for maximum pit depth (with $S_v + S_k$, Eq. 1), average pit depth (with S_{dr}/V_{vv} , Eq. 2), and pitted area percentage (with $S_{vk} \cdot V_{vv}/S_{dr}$, Eq. 3) were successfully developed for the pitting corrosion on carbon steel induced by the *D. vulgaris* (Chen and Ju, 2015). When analyzing the correlation between average pit depth and S_{dr}/V_{vv} , the pits with pit depth < 4 μm do not increase S_{dr}/V_{vv} significantly, so a minimum of 4 μm pit depth was selected during average pit depth calculation (Chen and Ju, 2015). This criterion was applied for both the chloride and *D. vulgaris* systems in the correlation development. As shown in Figure 3, the results of the current study confirmed that these correlations work very well for the pitting induced by chloride ions and for the pitting on carbon steel coupons with different levels of surface roughness. This finding significantly improves the potential applicability of these correlations to a wider range of pitting corrosion systems and conditions.

4.7.2. Pitting pattern four-phase diagram

Shown in Figure 4 are the pitting pattern four-phase diagrams with average pit depth as the y-axis and pitted area percentage as the x-axis. The diagrams were

generated using the IFM scanning results for coupons incubated with *D. vulgaris* or 3.5% NaCl for 3 or 21 days. These diagrams are useful to reveal the pitting patterns resulting from different pitting causes (*D. vulgaris* versus chloride) and different surface roughness levels. For the effects of *D. vulgaris* versus chloride, the SRB systems had significantly more scanning areas in Phases II and IV than the chloride systems on both polished (Figure 4 (a)) and unpolished (Figure 4 (b)) surfaces. Phases II and IV correspond to high pitted area percentages. The finding indicated that *D. vulgaris* was significantly more potent than chloride in initiating carbon steel pitting and causing higher pitted area percentages.

Regarding the surface roughness effects, on the polished surfaces, the few pitted areas on coupons from the chloride systems were all in Phases I and III (Figure 4 (a)) whereas the large number of pitted areas from the *D. vulgaris* systems were in all four phases, with many in Phases II and IV. On the unpolished surfaces, the majority of pitted areas from the NaCl systems were in Phase I, except one in Phase II and another in the transition between Phases I and III (Figure 4 (b)). There were clearly fewer Phase III areas compared to the pattern seen on the polished surfaces. A similar trend was found for the SRB-induced pitting: while there were many Phase III pitting areas on the polished surfaces, there were none on the unpolished surfaces (instead, pit clusters developed). This observation is consistent with the reports that metastable pits are easier to form on rough surfaces because of the lower pitting potential (thus, more areas in Phases I and II) while the metastable pit formed on smooth surfaces has higher chance to be activated into a stable pit (thus, more areas in Phases III) (Burstein and Pistorius, 1995; Sasaki and Burstein, 1996). Accordingly, with increasing exposure time, the dominant phase transition path on the polished surfaces appeared to be Phase I→III for the chloride systems and Phase I→III→IV for the SRB systems, whereas on the unpolished surfaces the common transition path might be Phase I→II for the chloride systems and Phase I→II→IV for the SRB systems.

As described above, the four-phase diagram can be used to distinguish pitting patterns caused by different pitting mechanisms, exposure times and surface roughness levels. However, it may sometimes be misleading if used for failure risk interpretation. For example, in Figure 4(a) the area with the largest average pit depth (33 μm) on polished carbon steel was found in the NaCl systems. On the contrary, the maximum pit depth was clearly higher in the *D. vulgaris* systems (46 μm) than in the NaCl systems (33 μm , Table 2). With close examination of the IFM scanned area having the highest average pit depth in the NaCl systems, the area had only a single narrow and deep pit. So, for that particular area the average pit depth was also the maximum pit depth. On the other hand, for the *D. vulgaris* systems, pit clusters were formed and the average pit depth could be substantially lower than the maximum pit depth due to the presence of

many shallower pits. Therefore, the pitting pattern diagram is not the best tool for failure risk indication.

4.7.3. Failure risk diagram

For indicating the failure risk associated with pitting corrosion, the diagram with maximum pit depth as the y axis and pit volume loss (V_{vv}) as the x axis was proposed to be more useful (Figures 4 (c) and (d)). The figures are plotted with V_{vv} values in a logarithmic scale. This rather arbitrary choice is made because the V_{vv} values are all very small for the chloride system and, when plotted in the normal scale, they mostly fall in a closely packed spot or on a single vertical line and, therefore, cannot be differentiated. The semi-logarithmic plots also allow more emphasis on the difference in maximum pit depth (shown in the normal scale), which is believed to be the most important factor for risk level prediction. The scanned areas with higher maximum pit depths are the more susceptible locations on the sample. When several scanned areas have similar maximum pit depths, the V_{vv} values in the x-axis, indicating the overall extents of pitting (total volumes pitted away), can further differentiate their risk levels as a secondary factor. (Intuitively, the area with higher pit volume loss is considered to have a higher risk level.) Thus, in the failure risk diagram, the bottom left corner has the lowest risk and the risk increases as the data move toward the top right corner.

As shown in Figures 4 (c) and (d), the systems with *D. vulgaris* gave higher maximum pit depth and pit volume loss (V_{vv}) than the NaCl systems, on both polished and unpolished surfaces. It is concluded that the *D. vulgaris* starving from organic electron donors is more damaging than the 3.5% NaCl solution under the anaerobic condition investigated. Furthermore, chloride mostly induced few deep pits, whereas both the maximum pit depth and pit volume loss were high in *D. vulgaris* systems due to deep pit cluster formation.

As for the effects of surface roughness, on the polished surface, there were two areas (Areas 1 and 2 in Figure 4 (c)) with maximum pit depth higher than 40 μm . Between these areas of similar maximum pit depths, Area 2 had higher pit volume loss (0.45 ml m^{-2}) than Area 1 (0.14 ml m^{-2}); therefore, Area 2 was considered to have the highest risk. On the unpolished side, there was only one area with maximum pit depth slightly higher than 40 μm (Area 3 in Figure 4 (d)). The pit volume loss of Area 3 (0.65 ml m^{-2}) was higher than those of Areas 1 and 2. As confirmed by the IFM 3D images (not shown), Area 3 contained many deep pits interspersed with many micro pits. Area 2 also had many deep pits but only few micro pits. Area 1 contained only two deep pits. The IFM images matched the order of pit volume loss in these areas very well.

In Figures 4 (c) and (d), for both the *D. vulgaris* and chloride systems the scanned areas on the polished and unpolished surfaces have similar ranges of pit volume loss but the maximum pit depth is generally higher on the polished side than the unpolished side. There are more pitted areas on the unpolished side (18 areas) compared with the

polished side (10 areas). This trend is consistent with that of pit density shown in Table 2, obtained from manual identification and counting of pits. The finding again suggests that higher pit density tended to form on the unpolished surface, whereas higher maximum pit depths were reached on the polished surface.

4.8 Effects of exposure time shown by pitting pattern and risk diagrams

Effects of exposure time were compared between 3 and 21 days (Figure 5). For the *D. vulgaris* system, the cells became starved of organic electron donors after about 2 days. So the pitting compared between 3 and 21 days was affected by the presence or absence of organics to the *D. vulgaris*. On the other hand, the abiotic chloride systems did not have this microorganism starvation effect. The scanned areas shown for the chloride systems were all the pitted areas with at least 1 pit with depth > 4 μm . For the *D. vulgaris* systems, all the pitted areas with pit depth > 4 μm (a manageably small percentage of all areas) at Day 3 were considered but at Day 21 most of the areas were pitted so only a small portion of representative areas were evaluated.

As shown by the pitting pattern diagrams, in the chloride systems most areas on the carbon steel surfaces were not pitted at Day 3 and only few areas appeared in Phase I with low average pit depths and pitted area percentages (Figures 5 (a) and (b)); after 21 days some Phase III areas (with very few deep pits) appeared on the polished surfaces and one Phase II area (with several shallow pits) appeared on the unpolished surfaces (Figures 5 (c) and (d)). Propagation of the chloride-induced pitting under the anaerobic condition was shown. Similarly, for the *D. vulgaris* systems (Figures 5 (a) through (d)), there were significantly fewer pitted areas at Day 3 than at Day 21. At Day 3, there were only 1 Phase III area on the polished surfaces and 3 Phase IV areas on the unpolished surfaces. Pits in these few localized areas had quickly propagated to Phases III and IV, with average depths > 10 μm . At Day 21, after *D. vulgaris* cells had been starved for 19 days, more areas appeared in Phases III and IV on the polished side, whereas on the unpolished side more areas moved into Phase IV but not Phase III. The organics-starving *D. vulgaris* cells were shown to be capable of causing formation of deep pits and clusters when they were surviving as attached biofilm on the metal surface (Chen et al., 2015). These conclusions derived from the pitting pattern diagrams cannot be seen from just the pitting parameters specified in the standard method (Table 2).

The exposure time effect on the risk level is clearly demonstrated by the failure risk diagrams shown in Figures 5 (e) through (h). For the chloride systems, after 3 days, neither maximum pit depth nor pit volume loss was high on the polished or unpolished surfaces. After 21 days the maximum pit depths and pit volume losses increased significantly in several areas, especially on the polished surface (Figures 5 (g) and (f)). With increasing exposure time (from 3 days to 21 days) the pitting-associated failure risk increased in the chloride system. A similar effect of exposure time in increasing the failure risk was found in the *D. vulgaris* system but the pattern of risk increase was

different on the polished and unpolished surfaces: On the polished side, both maximum pit depth and pit volume loss increased significantly (Figures 5 (e) and (g)); on the unpolished side, maximum pit depth did not change much whereas the pit volume loss increased significantly (Figures 5 (f) and (h)). The organics-starving *D. vulgaris* continued to contribute significantly to the increased pitting-associated risk level.

4.9. Significance of the methods

Obtaining the pitting parameters specified in the ASTM standard method (ASTM, 2005b) by IFM generally required significant time and manual effort in the past. And the average pit depths obtained by measuring depths of individually identified pits were associated with large standard deviations (Table 2). These difficulties limited the reported quantitative pitting corrosion data in the literature (Ilhan-Sungur et al., 2007; Rao et al., 2005). The methods used in this work allowed fast characterization of pitting by calculating percentage of pitted area and maximum and average pit depths from standard 3D surface parameters using Eqs. 1-3. An earlier study showed that the scan area did not significantly affect the outcomes of the methods (Chen and Ju, 2015). Further, two types of diagrams were generated: one for categorizing pitting patterns, the other for indicating risk associated with the pitting corrosion. Failure risk diagram is not expected to be affected by the scan area size because the maximum pit depth and V_w (pit volume loss per area) are independent of the scan area size (as long as the scanning resolution remains the same). Thus, the failure risk diagram can be very easily constructed using the parameters generated by reconstructing the full surface by combination of the individual partial surface scans (done with built-in capability of IFM). For example, in our study the whole coupon can be imaged by combining several individual images by IFM with 20x magnification. Then, for data analysis, 4 to 6 areas can be selected to cover the surface while excluding edges and other defect areas (such as the holes used for hanging the coupons in this study). Furthermore, as shown by the AR vs. AB diagrams (Figure 2 (a), (b) and Table 3), pits formed in the *D. vulgaris* and chloride systems on surfaces with different roughness had different pit morphologies but the proposed methods appeared to work well for all these pitting systems. 3D surface parameters were also obtainable by other equipment (i.e. 3D profilometer), which provided potential applicability of the method to other instruments.

The methods used in this study may also assist the development of online monitoring of pitting corrosion using, for example, electrochemical techniques. Several kinetic models for pit growth were proposed, based on correlations between current density, pit depth, pit radius, and exposure time (Szklańska-Smiałowska, 1986). Many researchers used the change of current density versus time to qualitatively indicate pit growth based on the established models (Isaacs and Kissel, 1972; Pistorius and Burstein, 1992; Punckt et al., 2004). Electrochemical noise measurement was also used to indicate occurrence of pitting (Cheng et al., 1999; Hladky and Dawson, 1981; Klapper

et al., 2011). But it is difficult to estimate pit depth quantitatively from current density measurements especially when different environments and/or pit shapes are involved, because most of the models are developed for certain assumed pit shape (cylindrical or spherical) and are valid only for the same material and environment (Szklańska-Smiałowska, 1986). The methods developed in this work offer a fast way to get pit depth and pitted area percentage information on sample surfaces. The information obtained from some representative samples can provide more realistic pitting characteristics for the intended monitoring target. These characteristics may be incorporated into advanced models to allow more accurate online monitoring using electrochemical techniques. Furthermore, the methods may assist gathering experimental data for pit modeling work (Alamilla et al., 2009; Caleyó et al., 2009; Laycock and Newman, 1997; Li et al., 2015; Melchers, 2005; Wang and Han, 2013).

5. Conclusions

The recently developed correlations, which used IFM-measured parameters to obtain maximum and average pit depths and pitted area percentage, were found to be applicable for the analysis of pitting occurring in several systems, including both polished and unpolished carbon steel surfaces exposed respectively to a SRB *D. vulgaris* and a 3.5% NaCl solution. Chloride ions induced predominantly conical pits while *D. vulgaris* cells induced pits of varying morphology: conical, hemispherical and cylindrical pits. The correlations worked well despite the differing pit morphology. This validation is important for expanding the use of the newly developed correlations. Further, in 21 days *D. vulgaris* caused the formation of deep pit clusters (Phase IV in the pitting pattern diagram) while chloride induced noticeably fewer deep pits along the surface scratches or defects. *D. vulgaris* also generated pits with larger maximum pit depth and pit volume loss V_w . For the effects of surface roughness, with increasing exposure time, the pits on polished surfaces tended to evolve through the transition path of Phase I→III→IV while those on unpolished surfaces transitioned through Phase I→II→IV. For both surfaces, the final transition to Phase IV, i.e., developing deep pit clusters, occurred only in the *D. vulgaris* system, not in the chloride system. The pitting pattern diagram was for the first time employed to follow and differentiate the pitting development paths in different corroding systems. Finally, in both *D. vulgaris* and chloride systems, the maximum pit depth was generally higher on the polished surfaces while the lost pit volumes were similar. Although numerous micro pits formed on the unpolished surfaces, the deeper pit clusters on the polished surfaces would likely be the sources of higher failure risk.

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Figure

Figure 1. Changes of *D. vulgaris* cell concentration, shown with optical density (OD), and pyruvate concentration in inoculated Postgate medium C in the absence of carbon steel (a) and pyruvate concentration change in the presence of carbon steel (b). Infinite focus microscope (IFM) images of the polished surfaces of carbon steel coupons that had been incubated under anaerobic condition for 21 days with 3.5% NaCl solution (c), and with the *D. vulgaris* culture in Postgate medium C (d), and for 43 days with abiotic Postgate medium C without carbon source (e). The area highlighted in (c) with the small white rectangle was enlarged as the arrow-indicated inset.

Figure 2. Diagrams of width/depth aspect ratio (AR) versus area-box parameter (AB) constructed for pit geometry evaluation for the carbon steel coupons corroded by exposure to the SRB *D. vulgaris* culture or 3.5% NaCl for 3 days and 21 days: (a) for polished surfaces; (b) for unpolished surfaces. (c) 2D (left) and 3D (right) views of IFM images for showing representative pit geometry observed in the *D. vulgaris* systems. The seven regions (I – VII) (Codaro et al., 2002) indicated in the diagrams corresponded to different pit geometry: (I) irregular pits, $AB < 0.5$; (II) conical pits, $0.5 < AB < 0.54$; (III) shape transition A, $0.54 < AB < 0.72$; (IV) hemispherical pits, $0.72 < AB < 0.86$; (V) shape transition B, $0.86 < AB < 1$; (VI) cylindrical pits, $AB = 1$; (VII) spherical pits, $0.72 < AB < 0.86$ and $1 < AR < 2$.

Figure 3. Correlations between (a) maximum pit depth and $S_v + S_k$, (b) average pit depth and S_{dr}/V_{vv} , and (c) pitted area percentage and $S_{vk} \cdot V_{vv}/S_{dr}$. Filled symbols are for data from polished surfaces and unfilled symbols from unpolished surfaces. Carbon steel coupons were incubated with 3.5% NaCl (●, ○) or the *D. vulgaris* culture in Postgate medium C (▲, △). Average pit depth can be estimated by S_{dr}/V_{vv} and pitted area percentage can be estimated by S_{vk} and S_{dr}/V_{vv} . Average pit depth calculations excluded micro pits (pit depth < 9 μm) when there was at least 1 significant pit (pit depth > 9 μm). If only micro pits were found, average pit depth was calculated based on all the pits with pit depth between 4 to 9 μm. To exclude effects of surface roughness on the area with only

micro pits, S_{vk} and V_{vv} values used in (c) had been subtracted by the corresponding values found on the non-pitted area on the same *D. vulgaris* or 3.5% NaCl incubated coupon. More details on average pit depth calculations were discussed elsewhere (Chen and Ju, 2015). S_k : height of the core material or kernel (μm), S_v : maximum valley depth (μm), S_{vk} : Mean depth of the valleys below the core material (μm), V_{vv} : valley void volume of the surface (ml m^{-2}), and S_{dr} : developed interfacial area ratio (%), = (actual surface area – projected surface area)/(projected surface area) $\times 100$.

Figure 4. Pitting pattern four-phase diagrams for (a) polished (filled symbols) and (b) unpolished (unfilled symbols) carbon steel surfaces; and pitting risk diagrams for (c) polished (filled symbols) and (d) unpolished (unfilled symbols) carbon steel surfaces. carbon steel coupons were incubated with 3.5% NaCl solution ($\bullet$, $\circ$) or *D. vulgaris* ($\blacktriangle$, $\triangle$) for 3, 21 or 43 days. In (c) and (d), V_{vv} (pit volume loss) was presented in a logarithmic scale. Each data point corresponded to an IFM scan with default scan area of 0.85 mm^2 at $20\times$ objective magnification. Arrows in (a) and (b) indicated the assumed phase transition pathways; arrows in (c) and (d) indicated the areas with the highest risk. Non-pitted areas were not shown in the figures. V_{vv} : valley void volume of the surface.

Figure 5. Pitting pattern four-phase diagrams [(a) – (d)] and pitting risk diagrams [(e) – (h)] generated for illustrating the effects of exposure time (3 versus 21 days), from the same pitting data shown in Figure 4. Carbon steel coupons with polished (filled symbols) and unpolished (unfilled symbols) surfaces were incubated with 3.5% NaCl solution (●,○) or *D. vulgaris* (▲,△) for 3, 21 or 43 days. For the *D. vulgaris* systems, the cells were starved of organic electron donor (pyruvate) after about 2 days. The scan areas for *D. vulgaris* systems shown in (c), (d), (g) and (h) were randomly selected pitted areas; almost entire surfaces were pitted after 21 days incubation with *D. vulgaris*.

Table 1. 3D surface parameters for representation of surface roughness of carbon steel coupons (a) before and (b) after 21 days *D. vulgaris* exposure.

Systems	Surface treatment	S_{pk} (μm)	S_{vk} (μm)	S_k (μm)
(a) before <i>D. vulgaris</i> exposure	Polished	0.29±0.08	0.47±0.06	0.89±0.19
	Unpolished	0.55±0.33	0.42±0.10	0.89±0.12
(b) 21 days <i>D. vulgaris</i> exposure	Polished	0.55±0.60	0.91±1.43	0.59±0.08
	Unpolished	0.79±0.65	1.88±1.65	0.87±0.27

Note: Coupons for (a) had been cleaned by acetone and ethanol sonication and those for (b) by Clarke’s solution. One side of coupons was not polished (“unpolished” surface). Reported roughness values were averaged from 35 scanned images for (a) and 124 scanned images for (b). Standard deviations indicated the roughness variations among different scanned areas. Large standard deviations indicated the scanned surfaces included rougher or pitted area(s). S_{pk} : mean height of the peaks above the core material, S_k : height of the core material (kernel), and S_{vk} : mean depth of the valleys below the core material.

Table 2. Important pitting parameters determined by measurements of individually identified pits for the anaerobic *D. vulgaris* and chloride systems investigated in this study

System	Surface treatment	Time (day)	Pit density (pits m ⁻²)	Maximum pit depth (μm)	Average pit depth (μm)	Average pit width (μm)
<i>D. vulgaris</i>	Polished	3	1.76×10^5	27	9 ± 7	46 ± 32
		21	4.78×10^5	46	12 ± 9	55 ± 17
	Unpolished	3	1.10×10^6	37	7 ± 6	52 ± 19
		21	3.00×10^7	41	11 ± 9	60 ± 19
3.5% NaCl	Polished	3	2.71×10^4	15	5 ± 5	29 ± 12
		21	3.44×10^4	33	6 ± 6	36 ± 17
	Unpolished	3	1.98×10^5	14	4 ± 4	42 ± 20
		21	2.72×10^5	24	8 ± 4	46 ± 19

Table 3. Percentage of different types of pit geometry formed in the *D. vulgaris* and chloride systems

Systems	Surface treatment	Time (day)	Percentage of different types of pit geometry (%)					
			Irregular	Conical	Transition		B	Cylindrical
					A	Hemispherical		
<i>D. vulgaris</i>	Polished	3	5	40	35	1.7	5	13.3
		21	5.0	35.6	24.8	0.0	5.9	27.7
	Unpolished	3	8.6	56.8	25.9	3.7	1.2	3.7
		21	4.0	37.6	22.8	6.9	7.9	20.8
3.5% NaCl	Polished	3	14.9	28.4	55.2	1.5	0.0	0.0
		21	6.3	62.5	18.8	0.0	4.5	8.0
	Unpolished	3	28.9	39.	31.6	0.0	0.0	0.0
		21	14.2	54.2	24.2	0.0	6.7	0.8