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Can Acid Producing Bacteria Be Responsible for Very Fast MIC Pitting?

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ABSTRACT

So far, laboratory experimental pitting tests and published literature on microbiologically influenced corrosion (MIC) have overwhelmly focused on sulfate reducing bacteria (SRB) that usually respire on sulfate (terminal electron acceptor) because SRB are often found at pitting sites. Many laboratory pure-culture SRB pitting data have been reported and they are often less than or not much greater than 1 mm/year. There are also some limited data available for nitrate reducing bacteria (NRB) that respire on nitrate or nitrite. Dedicated laboratory studies are lacking on anaerobic corrosion by acid producing bacteria (APB) that undergo anaerobic fermentation instead of anaerobic respiration in the absence of an external terminal electron acceptor such as sulfate and nitrate. Some failures in pipelines carrying crude oil and produced water, purportedly due to MIC, have been reported in the literature indicating very high pitting rates (as high as 10 mm/year) that are much higher than the short-term laboratory MIC pitting rates for SRB. The pipeline failure cases discussed in this work occurred in relatively low sulfate conditions. This work explored the possibility of very high MIC pitting rates due to organic acids (represented by acetic acid) and acidic pH corrosion through mechanistic modeling to show that APB are capable of very fast MIC pitting and mass transfer limitation on sulfate diffusion from the bulk-fluid phase to the biofilm cannot support very fast pitting caused by sulfate reduction in a low sulfate concentration environment. More efforts should be devoted to APB instead of focusing too much on SRB.

Key words: APB, SRB, MIC, mechanistic model, anaerobic respiration, anaerobic fermentation.

INTRODUCTION

Microbiologically influenced corrosion (MIC) is an increasingly important issue in the oil and gas industry as well as other industries. Sulfate reducing bacteria (SRB) are often blamed for MIC primarily because of their frequent presence at corrosion sites in corrosion cases that are believed to be MIC related[1]. Acid producing bacteria (APB) have also been known to be involved in MIC. However, the overwhelming majority of MIC literature and laboratory investigations were focused on SRB, leading to the misconception that APB play only a minor role in MIC. MIC forensics is poorly practiced at present compared to the stringent pathogen identification in the medical field that relies on the very methodical Koch's postulates[2]. The presence of a microbe at a corrosion site does not automatically prove its culpability because microbes are everywhere under field conditions. Published MIC field cases[3-5] often depended on a process of elimination to narrow down the suspected cause to MIC, sometimes by relying on a general belief that conventional chemical corrosion tends to have a far more uniform environment. Thus, pipeline failures involving only one or a few large pits in a long pipe section were believed likely due to MIC because biofilm formation was opportunistic, even in the absence of any convincing microbiological evidence. This uncertainty necessitates laboratory MIC testing with defined microbiological conditions to provide clues.

It is well known in microbiology that there are two distinct types of anaerobic metabolism[6]. The first type is anaerobic respiration in which an external (non-oxygen) oxidant such as sulfate, thiosulfate, sulfite, sulfur, nitrate, nitrite, CO_2, etc. serves as the terminal electron acceptor to adsorb the electrons released from organic carbon oxidation (or hydrogen oxidation by methanogens and some SRB among others). The electron transport chain in anaerobic respiration provides energy for ATP (an energy-storage molecule) synthesis. In laboratory culturing of SRB, lactate is often used as the electron donor and sulfate as the terminal electron acceptor to provide energy needed for SRB growth. Xu et al.[7] showed that starting with the same biofilms, when *Desulfovibrio vulgaris* (ATCC 7757) was starved of organic carbon, this SRB pitted carbon steel more aggressively. This suggested that some sessile SRB cells switched from organic carbon oxidation to iron oxidation, i.e., oxidation of elemental Fe(0) to ferrous Fe(II) ion. In the absence of an organic carbon and other electron donors (such as H_2), elemental iron becomes a substitute fuel for energy production[7]. Unlike lactate oxidation, iron oxidation does not produce any organic carbons that can be used in organic synthesis needed for growth. Thus, iron is merely a fuel rather than food for SRB. SRB do not "eat" iron, but they extract energy from it by coupling its oxidation with sulfate reduction. Energy is always needed by microbes because even when they are not growing their survival requires maintenance energy[6].

The second type of anaerobic metabolism is anaerobic fermentation. In the absence of an external acceptor, fermentative microbes such as APB and SRB strains that are capable of fermentative growth oxidize an organic carbon and produce ATPs through substrate-level phosphorylation. No external electron acceptors are required because cells achieve redox balance by producing their own electron acceptors that are organic carbons derived from the carbon source[6]. Anaerobic fermentation products typically are organic acids such as volatile fatty acids (lactic acid, acetic acid or HAc, etc.) and alcohols[6]. Due to organic acid production, the pH underneath an APB biofilm can be considerably lower than pH 7. It is said that the pH differential between the bulk-fluid and the bottom of a biofilm can be greater than 2. Vroom et al.[8] located an area with pH < 3 in a biofilm adjacent to areas with pH > 5 using the two-photon excitation microscopy technique. Some APB can produce alarmingly large amounts of organic acids. Pope et al.[9] found that the broth of a mixed-culture APB "contained organic acids totaling 12,000 ppm. Acetic acid was at 4000 ppm." They did not indicate broth pH and whether these were free (undissociated) acid concentrations or not. The concentrations were very likely total concentrations including free acids and dissociated acids because their data came from ion chromatography.

The low pH in an APB broth is caused by the protons released by the organic acids. Because these organic acids are weak acids, the majority of them are still in the free acid form. They are corrosive because the reduction of the acids combined with iron oxidation is thermodynamically favorable and

kinetically not retarded. They are a serious threat because the organic acid concentrations can be much higher than proton concentrations. Their corrosive ability dwarfs that of protons due to their much higher concentrations of undissociated organic acids compared with proton concentrations. For example, a pH 2 acetic acid solution is much more corrosive than a pH 2 sulfuric acid solution[9]. The acetic acid solution at pH 2 contains a very large free acetic acid concentration while the pH 2 sulfuric acid solution contains no undissociated sulfuric acid in the liquid because sulfuric acid is a very strong acid. The free acetic acid can re-supply protons that are consumed by corrosion.

Bhat et al.[3] documented the failure of a new 8-inch ID pipe (6.4mm thickness) that failed in only 8 months at 45°C, corresponding to an averaged pitting rate of 9.6 mm/year assuming no initial delay in the onset of corrosion. The untreated pipeline carried oil and produced water (as high as 70% water-cut) at pH 5.1. Both APB and SRB were found present in the pipeline fluid that contained 1500 ppm acetic acid and no detectable sulfate. Samant et al.[4] reported that an offshore 16-inch ID (22.2 mm thickness) pipeline carrying well fluid (oil/gas/water) failed in 2.5 years at 41°C very likely due to MIC. In this case, the pitting rate averaged 8.9 mm/year. The pipeline fluid contained 410 ppm sulfate with a water-cut of 75%. In both cases, the roughly 4 psi CO_2 partial pressure could not account for the severe corrosion rate. Strickland et al.[5] investigated the well-known 1991 Lost Hills, CA oil and water gathering system MIC failure that occurred 18 months after startup with an averaged pitting rate of 6.8 mm/year. Coupon tests in the pipeline showed that the coupons suffered no pitting in the first month, but a 7.6 mm/year pitting rate was observed in the second month. No corrosion of coupons in turbulent areas occurred, suggesting that CO_2 corrosion was not a factor. All the three cases above involved constant water-wetting condition and no oxygen. These conditions were favorable for anaerobic microbial biofilms to thrive in the presence of organic nutrients. The constant water-wetting condition allows a much larger variety of microbes to flourish than the oil-wetting or the intermittent water-wetting condition, thus increasing the possibility of a very corrosion biofilm on the pipe wall. As water-flooding is more frequently used to increase well pressure in older wells, water-wetting condition for an oil transport pipeline is becoming more common than ever. The risk for fast MIC pitting failure is undoubtedly heightened.

This work showed that these very fast purported MIC pitting rates could not be accounted for by SRB pitting alone because in these systems with zero or a low sulfate concentration, sulfate diffusion from the bulk- fluid phase to the biofilm was far from sufficient to sustain the high MIC pitting rates. APB was likely the primary suspect in this kind of fast MIC pitting failures.

THEORY AND MECHANISTIC MODELING OF MIC DUE TO SRB AND APB

Gu et al.[10] proposed a new theory called Biocatalytic Cathodic Sulfate Reduction (BCSR) theory based on bioenergetics. They departed from the tradition of corrosion engineers who searched for a physical anode and a cathode when studying MIC mechanisms. Instead, they suggested that MIC by SRB is due to the utilization of electrons from iron oxidation by sulfate reduction by SRB cells as shown below,

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (1)$$

$$SO_4^{2-} + 9H^{+} + 8e^{-} \rightarrow HS^{-} + 4H_2O \quad (2)$$

This electron utilization requires the biocatalysis of an SRB biofilm for sulfate reduction. Instead of a physical anode and a cathode, they proposed that an anodic reaction (iron oxidation) and a cathodic reaction (sulfate reduction) coupled together cause MIC. The word “cathodic” here overlaps with the word “reduction,” both indicating that the half reaction is an electron utilization reaction. The use of “cathodic” is only for easier understanding by corrosion engineers. Reaction (2) happens in the cytoplasm inside SRB cells[11] while Reaction (1) happens outside SRB cells. There is no physical cathode, but rather sulfate reduction in cytoplasm. Reaction (2) should not be interpreted as automatically reducing the acidity of an SRB culture because other reactions in the SRB cells also

involve protons at the same time. They can lead to zero net proton consumption[12]. Elemental iron is considered the electron donor while sulfate is known as the terminal electron acceptor for sulfate respiration. The combined redox reaction is thermodynamically favorable (energy producing), but sulfate reduction is kinetically retarded by a high activation energy unless there is biofilm catalysis. Reaction (1) does not require biocatalysis, but it won't proceed if Reaction (2) is blocked. In lab tests, a polished carbon steel coupon in a deoxygenated SRB culture medium remains unpitted and shiny unless an SRB seed culture is introduced. Iron oxidation occurs beneath an SRB biofilm and supplies electrons to the biofilm for sulfate reduction either directly or indirectly. Iron oxidation can couple with water or proton reduction to produce H_2 (just as in chemical corrosion without biocatalysis or a biofilm). H_2 is well known as an electron donor that can be used as an energy source for culturing (hydrogenase-positive) SRB. SRB cells benefit from the thermodynamically favorable redox reaction (oxidation of H_2 coupled with sulfate reduction) because energy is produced. This is just one example among several different mechanisms for SRB to transport the electrons from outside the cells to the cytoplasm. This example is consistent with the classic cathodic depolarization theory (CDT)[13,14] that is valid for hydrogenase-positive SRB. When the local SRB cells on an iron surface in a biofilm are starved of organic carbon due to a lack of organic carbon in the bulk-fluid phase or due to diffusional limitation, the cells will switch from organic carbon oxidation to iron oxidation to obtain maintenance energy for survival[7]. In fact, Fe has a standard potential of –447mV that is close to the –430mV standard potential of lactate that is often a favored organic carbon for SRB. Both are more negative than the –217 mV standard potential for sulfate reduction[15]. This means both iron oxidation and lactate oxidation can donate electrons for sulfate reduction with concomitant energy production. All potentials in this work are relative to the standard hydrogen potential.

Although other SRB MIC mechanisms have been proposed such as the cathodic FeS film corrosion theory[16], it is undisputed in SRB bioenergetics that sulfate acts as the terminal electron acceptor[12]. This means electrons released by iron oxidation are ultimately absorbed by sulfate reduction in the cytoplasm of the SRB cells. The iron sulfide film beneath an SRB biofilm is not an electron sink. It's in the path of electron transport route from iron surface to the biofilm. Different forms of iron sulfide have different abilities to transport the electrons across the mineral film. It is well known that the Mackinawite form passivates the iron surface against corrosion. If a non-passivating semi-conductive iron sulfide film is present, electrons will be allowed to pass through the mineral film into the SRB biofilm resulting in corrosion. Some hydrogen sulfide ions (HS^-) produced by SRB respiration will be converted to hydrogen sulfide in a reversible reaction ($HS^- + H^+ \leftrightarrows H_2S$)[10]. H_2S can cause corrosion, but it can also produce protective Mackinawite depending on its local concentration.

The BCSR theory can be readily extended to the Biocatalytic Cathodic Nitrate Reduction (BCNR) theory for nitrate reducing bacteria (NRB) that respire on nitrate. If the end product for nitrate reduction is nitrogen, the cathodic reaction is written as follows.

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \quad (3)$$

Reaction (3) has a standard potential of +760mV, much more positive than that of sulfate reduction[15]. This means NRB can potentially be much more corrosive than SRB. However, nitrate is not typically present at a significant concentration in systems not involving nitrate injection for souring control or water contaminated with agricultural run-off.

Instead of using the term SRB, Xu et al.[7] suggested a more general term XRB (X reducing bugs including methanogens that are archaea) where X stands for any non-oxygen oxidant such as sulfate, nitrate, nitrite, sulfur, CO_2, etc. Thus, the MIC theory can be generalized as Biocatalytic Cathodic X Reduction (BCXR) theory that is suitable for MIC due to anaerobic respiration. When the BCXR mechanism is involved in MIC, the motive for the XRB is to harvest energy and the attack on iron is intentional requiring active biofilm catalysis for the reduction reaction (e.g., sulfate reduction). We may call this Type I MIC mechanism that has a direct bioenergetic benefit to the biofilm. The Type II MIC mechanism is the attack by secreted metabolites such as organic acids. It is possible that microbes do

not directly benefit bioenergetically because the thermodynamically favorable redox reaction (iron oxidation coupled with acid or proton reduction) occurs outside cells without any need for biocatalysis. Energy released by the corrosion process is dissipated as low-grade heat outside the cells. One possible exception is the utilization of H_2 (produced by proton or organic acid reduction when coupled with iron oxidation) by methanogens and some SRB species. In such a case, it cannot be ruled out that cells actively push the corrosion forward for their own gain because these sessile cells in the biofilm can benefit from the production of the energy molecule (H_2). Thus, in this case Type II mechanism also has a motive and can be intentional. Apart from the primary example of Type II MIC attack due to anaerobic fermentation products (e.g., organic acids) secreted by APB, corrosion by exopolymeric substances (EPS) also belongs to this type. Oxidants such as protons and uronic acids in EPS may be directly responsible for MIC[17]. An exception is that EPS with cells inactivated can still cause MIC due to cell-free enzyme catalysis[18]. However, this may be an insignificant carry-over case from Type I. Due to a lack of viable cells, such MIC will be limited in damages because the dead biomass will eventually lose enzyme activities or direct contact with a pit bottom surface as the pit grows deeper. Copper corrosion by SRB belongs to Type II rather than Type I. Unlike the Fe^{2+}/Fe standard potential (-447mV), the Cu^{2+}/Cu, Cu^{+}/Cu standard potentials (342mV and 521mV, respectively) are much more positive such that direct Cu oxidation to Cu^{2+} or Cu^{+} ion will not happen. Coupling copper oxidation with sulfate reduction is not thermodynamically favorable. However, the direct reaction of copper with H_2S, an extracellular metabolite produced by SRB, is thermodynamically favorable and requires no biocatalysis. MIC mechanisms other than Types I and II are also possible such as MIC due to iron oxidizing bacteria (IOB) that oxidize Fe^{2+} to Fe^{3+}.

The effect of HAc on CO_2 chemical corrosion was studied by George et al.[19]. They obtained a corrosion rate close to 10 mm/year for X65 carbon steel at 40°C and pH 4 with 100 ppm total acetates (HAc and Ac^- combined) in the bulk liquid with bubbling CO_2 in a rotating cylinder (1000 rpm) glass cell. In MIC, it is well known that APB can secrete various organic acids. In practice, these organic acids are often expressed as HAc equivalent because it is impractical to account for all the organic acids individually. HAc is a weak acid. Its disassociation to acetate ion and proton is reversible,

$$HAc \quad \leftrightarrows \quad H^+ \quad + \quad Ac^- \tag{4}$$

The molar concentration-based equilibrium constant for this reaction is,

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} \tag{5}$$

in which K_a is a function of absolute temperature T in Kelvin[20],

$$K_a = 10^{-6.66104+0.0134916T-0.0000237856T^2} \tag{6}$$

If a pH is maintained by neutralizing some protons, the concentration of noncorrosive Ac^- can increase greatly due to Reaction (4). On the other hand, if some protons are from other sources, Ac^- concentrations will be lower. [Ac^-] can come from sources other than Reaction (4), and its value impacts the availability of undissociated HAc that is corrosive.

Both proton and undissociated HAc can be reduced to accept electrons from iron oxidation[21],

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{(Proton reduction)} \tag{7}$$
$$2HAc + 2e^- \rightarrow 2Ac^- + H_2 \qquad \text{(Free acetic acid reduction)} \tag{8}$$

Because Reaction (4) is extremely fast, it is not possible to distinguish the reduction of HAc from the reduction of proton according to Garsany et al.[22] This means HAc behaves like a proton reservoir that

releases protons on demand for proton reduction. For simplicity in APB MIC modeling in this work, it was assumed that acidity underneath the biofilm is solely due to the dissociation of HAc. Apart from APB, some SRB can also produce small amounts of organic acids if these SRB are present in the biofilm consortium. Because HAc is a weak acid, at an acidic pH there is far more free HAc than H^+ available in molar quantities for reduction. Thus, iron oxidation due to HAc reduction is far more severe than proton reduction[21].

Both charge transfer resistance and mass transfer resistance are considered in the BCSR model[10]. The charge transfer resistance $1/i_{ct}$ can be obtained using the Butler-Volmer equation below that treats all half reactions such as Reactions (1) and (2) as reversible reactions,

$$i = i_0 \cdot \left\{ \exp\left[\frac{(1-\alpha)\cdot n \cdot F}{R \cdot T} \cdot (E - E_{eq}) \right] - \exp\left[-\frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot (E - E_{eq}) \right] \right\} \quad (9)$$

i: current density, A/m^2
i_0: exchange current density, A/m^2
E: (corrosion) potential, V
E_{eq}: equilibrium potential, V
F: Faraday constant, Coulombs/mol
n: number of electrons involved in an electrodic reaction
R: universal gas constant, J/(mol-K)
T: absolute temperature, K
α: symmetry factor, dimensionless

The exchange current density i_0 in the Butler-Volmer equation for the BCSR reaction is defined as the biofilm aggressiveness. This is an electrochemical parameter equivalent to the rate constant in chemical reaction kinetics. Without biofilm catalysis, i_0 for suflate reduction would be extremely small, meaning the reaction is kinetically retarded and will not proceed at any appreciable speed due to a high activation energy barrier. An SRB biofilm can greatly increase this parameter by lowering the activation energy. This parameter represents the catalytic ability of a biofilm to help remove electrons from an iron surface for utilization in biofilm anaerobic respiration. If the potentials involved in the redox reaction consisting of Reactions (1) and (2) were pressures in a pressure-driven water flow system, the role of SRB biofilm catalysis would be analogous to de-blocking the pipe to allow flow to proceed. The exchange current density for the biofilm may vary with many parameters such as sessile cell density directly on the iron surface, their enzyme activities at different temperatures and what type of iron sulfide film is present on the iron surface. It is calibrated from SRB pitting data using a software program based on the BCSR model[10].

The classic eletrochemical kinetics theory dictates that the anodic current density should equal to the overall cathodic current density that covers proton reduction, HAc reduction and sulfate reduction as shown below in which $i_{a(Fe)}$ is calculated from Eq. (9) without mass transfer resistance,

$$i_{a(Fe)} = i_{c(H^+)} + i_{c(acetic\_acid)} + i_{c(SO_4^{2-})} \quad (10)$$

The cathodic current density for sulfate in the equation above is related to the cathodic charge transfer current density that is calculated from the Butler-Volmer equation and the cathodic mass transfer current density as shown below according to the classical electrochemical kinetics frequently used in mechanistic CO_2 corrosion modeling[23],

$$\frac{1}{i_{c(SO_4^{2-})}} = \frac{1}{i_{lim(SO_4^{2-})}} + \frac{1}{i_{ct(SO_4^{2-})}} \quad (11)$$

The ratio of the two terms on the right hand side of the equation above is the mass transfer resistance to charge transfer resistance. As a pit grows, this ratio becomes larger because the distance for sulfate diffusion increases. For deep pits, mass transfer resistance dominates because sulfate in the bulk fluid must diffuse through a long distance to reach the pit bottoms. The following equation can be used to describe mass transfer of sulfate across the biofilm,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) + R_c \quad (12)$$

C: concentration of chemical species j in biofilm, mol/m^3
D: sulfate diffusion coefficient in biofilm, m^2/s
R_c: rate of consumption of sulfate by sessile SRB cells in the bulk of biofilm, mol/(m^3·s)

R_c is a negative value indicating consumption of sulfate by the bulk sessile SRB cells in the biofilm. This consumption requires organic carbon as electron donor, because electrons from iron oxidation can only reach the sessile cells near the iron surface (often a monolayer of cells only) and they cannot "swim" to the bulk of the biofilm. The mass transfer current density is obtained from the following equation from the sulfate concentration gradient on the iron surface,

$$i_{lim(SO_4^{2-})} = -nFD\frac{\partial C}{\partial x} \quad (13)$$

In the equation above, n=8 because reduction of each sulfate ion consumes 8 electrons. $i_{a(Fe)}$ obtained from Equation (10) can be converted to corrosion rate CR (pitting rate in this 1-D model) based on the following equation[10],

$$CR = \frac{M_{Fe}}{2F\rho_{Fe}} i_{a(Fe)} \quad (14)$$

It can be expressed as the following equation for typical iron and mild carbon steel[24],

$$CR\ (mm/y) = 1.155 i_{a(Fe)}\ (A/m^2) \quad (15)$$

APB corrosion studies are lacking and there are no published correlations to calculate the pH and HAc concentration underneath biofilms. The HAc corrosion mechanism in this work is a simplistic one without consideration for CO_2 involvement[25], scale or film formation that may inhibit the corrosion. Instead of modeling the mass transfer and acid production within the biofilm that require many unavailable parameter values, it is assumed that a constant acidic pH and a constant free HAc concentration at the bottom of a pit are maintained. Doing so requires that diffusion of proton and HAc within the biofilm is sufficiently fast to accommodate their reduction reactions on the iron surface, thus mass transfer resistances of proton and HAc are not considered in the model. It also requires that the metabolic activities of the biofilm should be sufficiently fast to provide the protons and HAc molecules to sustain the specified local pH and acetic acid concentration, and to compensate for the loss due to diffusion into the bulk fluid. This again requires that there is sufficient organic carbon as food for the biofilm to produce the organic acids. Thauer et al.[15] mentioned that the prevailing hydrogen partial pressure is between 1 to 10 Pa in sediments. However, with significant proton reduction and HAc reduction locally, hydrogen partial pressure could be much higher. There is also a possibility that some hydrogen may be consumed by SRB or methanogens in the biofilm. Due to a lack of literature and lab data on the local hydrogen partial pressure on the iron surface, 1 bar is assumed in the Nernst equation

for proton reduction potential calculation. A lower hydrogen pressure results in a more positive E_{eq} for proton reduction that means a larger driving force for corrosion.

RESULTS AND DISCUSSION

The extended BCSR model with proton and HAc reductions was solved numerically in the MIC prediction software known as MICORP* Version 1.5.1 developed by the author. Figure 1 shows that with 400 ppm (4.17 mM) sulfate in the bulk-fluid phase and no free HAc at pit bottom (pH 7) at 45°C, the maximum predicted pitting rate is around 3.3 mm/year even with an extremely large SRB biofilm aggressiveness (log_{10} scale) of –6. The upper end laboratory strain SRB biofilm aggressiveness for SRB is around –12 which would give a pitting rate of 1.4 mm/year for 28 mM sulfate (typical seawater).

In Figure 1, when the aggressiveness increased beyond –8, pitting did not increase much. This was because mass transfer of sulfate was limited due to a relatively low sulfate concentration above the SRB biofilm. As a pit grew, the distance for sulfate in the bulk fluid to diffuse to the bottom of the pit increased and this further reduced the ability of the biofilm to oxidize iron at the pit bottom. Figure 2 shows that mass transfer resistance became increasingly dominating over time, as the pit grew deeper. In Figure 2, the sulfate consumption by the bulk sessile SRB cells with concomitant organic carbon oxidation[10] is not considered in the simulation. If it were considered, there would be less sulfate that reached the iron surface, meaning the corrosion rate due to BCSR could be even smaller. A sulfate diffusivity of $1.2x10^{-9}$ m^2/s in the biofilm at 45°C was used in the simulation in this work. It was calculated from the $0.7x10^{-9}$ m^2/s diffusivity value for sulfate in the biofilm at 25°C based on the Stokes-Einstein equation that says diffusivity is directly proportional to absolute temperature and inversely proportional to liquid viscosity[26]. The sulfate diffusivity in water is $1.06x10^{-9}$ m^2/s at 25°C according to Stewart[27]. $0.7x10^{-9}$ m^2/s for sulfate diffusivity in the biofilm reflects a 34% discount. The discount depends on the biofilm density[10] that is not easily available.

Figure 3 shows that when a pit bottom pH of 3.6 is maintained, the one-year pit depth was slightly greater than 10 mm. The corresponding free HAc concentration [HAc] was 226.3 ppm (equivalent to $3.77x10^{-3}$ M) calculated from Eq. (5) with $K_a=1.68x10^{-5}$ M at 45°C and assuming $[Ac^-]= [H^+] = 2.51x10^{-4}$ M, equivalent to $[Ac^-]$=14.8 ppm. This depth remained unchanged when the biofilm aggressiveness was less than or equal to –10. This means that the contribution from the BCSR effect was negligible compared to HAc corrosion and proton corrosion. At pH 3.6, $[H^+] = 2.51x10^{-4}$ M, that was 15 times smaller than [HAc] = $3.77x10^{-3}$ M. The contributions from HAc and H^+ to the total corrosion rate remained roughly 94.5% and 5.5%, respectively during the 365 days based on the cathodic current density values (see Eq. (10)) calculated by the MIC software. The ratio of the two percentages was 17.2, not too far from the ratio of HAc and proton concentrations in this case. The simulation results proved that HAc is far more corrosive than proton because [HAc] is much larger than $[H^+]$. This is characteristic of organic acid corrosion that involves weak acids.

CONCLUSIONS

A mechanistic MIC model involving sulfate, proton and HAc reductions was used to prove that BCSR by SRB under a low sulfate concentration condition could not account for a very fast pitting rate, while APB corrosion could. Based on the HAc corrosion theory and published field cases, it is reasonable to believe that severe APB attacks can lead to pipeline failures in less than a year if constant water wetting is an operating condition. As water-flooding is increasingly used to increase well pressure, water-wetting condition for an oil transport pipeline is becoming more common than ever. Alarmingly fast MIC pitting by APB is a realistic threat in water-injection pipelines and water-wetted oil transport pipelines. The parameters in the modeling of proton and acetic acid attacks in this work can be refined

* Trade name

by calibration using experimental and field data to predict local pH and acetic acid concentration more accurately corresponding to a pitting rate, or vice versa. This work is a theoretical study to encourage a thrust in the experimental investigation and more accurate mechanistic modeling of MIC by APB. It calls for the awareness of potentially very fast pitting by APB. Attention should also be paid to NRB MIC because it involves a much larger corrosion potential (E_{corr}).

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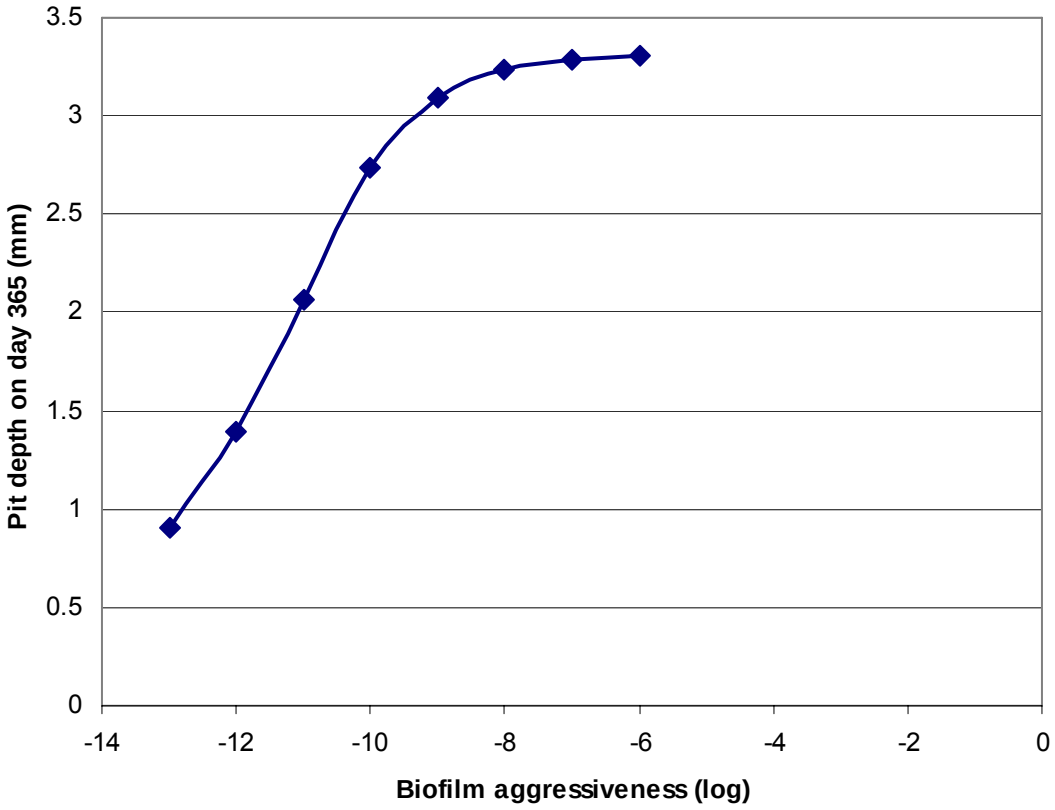

Figure 1: Simulation results based on 4.17 mM sulfate, pH 7 and an initial SRB biofilm thickness of 0.1 mm at 45°C.

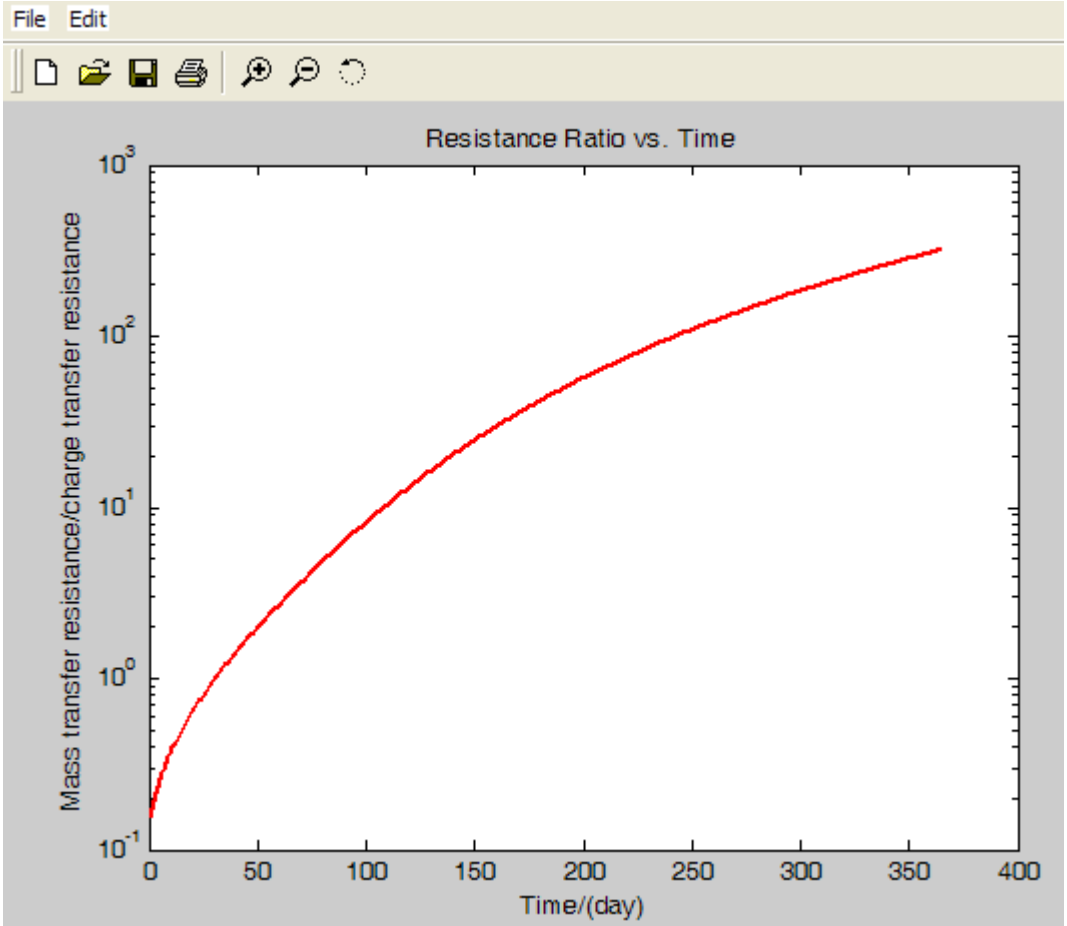

Figure 2: Simulated data (corresponding to Figure 1 with a fixed biofilm aggressiveness of –9) showing mass transfer resistance domination when pit grows.

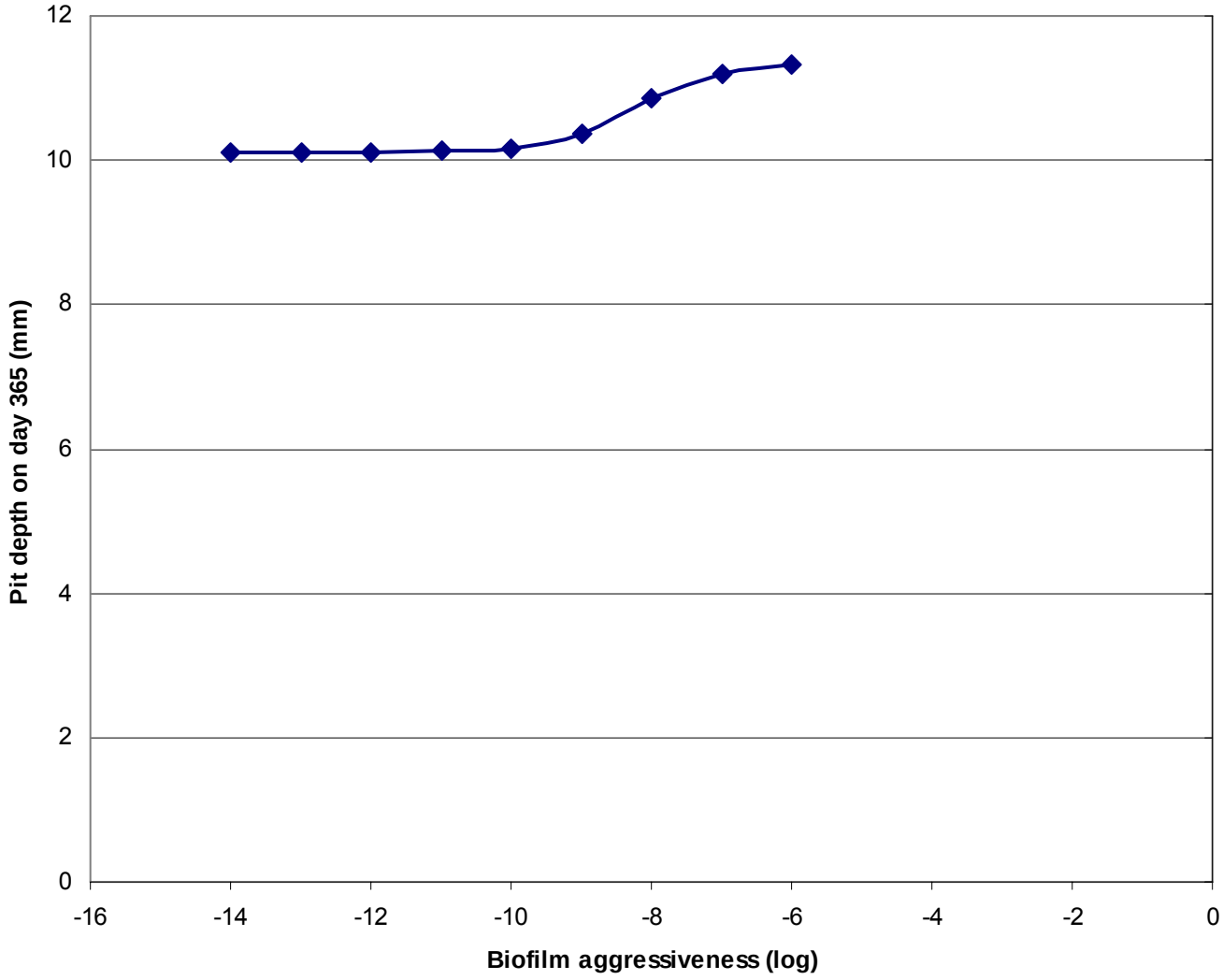

Figure 3: Model predicted pit depths for pH 3.6, 226.3 ppm free HAc, 4.17 mM sulfate and an initial SRB biofilm thickness of 0.1 mm at 45°C.