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Physicochemical Description of Refinery High Temperature Naphthenic Acid Corrosion

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ABSTRACT

Refinery high temperature naphthenic acid corrosion is known to generate oil soluble iron naphthenates and solid iron oxide as corrosion products. Associated chemical reactions have been written for a long time but are barely sufficient to resolve the comprehensive mechanism necessary to model their kinetics. A mechanism for naphthenic acid corrosion is proposed to be proceeding via formation of active intermediate by adopting the Lindemann-Hinshelwood approach. The rate law for the calculation of pure naphthenic acid corrosion rate was derived using a pseudo steady state hypothesis which could simulate laboratory corrosion data reported in the literature. The rate equation was also validated by experimental corrosion tests conducted in a high temperature flow-through reactors for carbon steel using a model oil solution of petroleum derived acids by manipulating solution concentration and temperature. Also, the formation of the solid iron oxide is proposed to be a result of the decay of active intermediate as an alternative mechanism in contrast with the currently accepted thermal decomposition pathway.

Key words: Naphthenic acid corrosion, Corrosion Mechanism, Kinetics

INTRODUCTION

The mechanism of high temperature naphthenic acid corrosion in crude distillation units of oil refineries remains poorly understood despite large-scale collaborative efforts. It has never been more urgent to be able to predict this corrosion due to the economic interest of oil refineries in processing cheaper high acid containing crudes but a lack of confidence in the capability of current prediction models. Moreover, a quite similar trend in corrosion rate is also expected in high temperature conversion of biofuels due to magnitudes of higher concentrations of organic acids therein.[1]

The limited success of foregoing investigations can be owed partly to the phenomenological aspects of this corrosion itself. For instance, concentration of naphthenic acids is essential to compute the corrosion rate using a model rate expression. However, thermal decomposition of naphthenic acids, at rates often unknown, makes it difficult to estimate the concentration of remaining acids.[2–6] Both iron and iron oxide catalyze decomposition of these acids[7] which further compounds analytical challenges. One may consider measuring concentrations of decomposition products with respect to time for the analysis of side reactions, but it is not trivial due to instrumental limitations for *in situ* concentration measurements. Intermittent sampling during the autoclave test would disturb the thermodynamic state of the system. Also, naphthenic acids tend to separate into the vapor phase due to their relatively high vapor pressure.[8,9] Another important aspect is the variety of molecular structures of organic acids with different reactivities in any crude oil.[3,6,10] Besides the dissolution of steel, a secondary mechanism of formation of iron oxide near the steel surface has also been observed.[10,11] In high temperature corrosion tests using a solution of only model acids, iron oxide does not seem to provide much protection against further corrosion. Also, there is no experimental data available on the growth rate of this iron oxide layer since it is difficult to quantify. Finally, naphthenic acid corrosion is always accompanied by sulfidation corrosion which adds further to the analytical complexity. Same as iron oxide, the protectiveness of an iron sulfide layer is also highly debatable.[9]

There are several complexities related to analyses of experimental data. While conducting corrosion experiments in a pilot scale loop or traditional high temperature autoclave, measured corrosion rate results from the contribution of all the aspects stated above. Evaluation of all the associated reactions using measurement of just corrosion rate essentially would involve several hypotheses which cannot be tested easily. In this case, isolated experiments pursuing individual phenomena are most reliable for understanding the mechanism but often not feasible to conduct. The values of reaction rate constants, diffusivities, or similar coefficients for current models estimated by isolated experiments have been unable to predict field corrosion rates with acceptable accuracy. Estimation of model coefficients by regression over field data might seem to be a solution to this problem, but then it defeats the whole purpose of developing a mechanistic prediction model, which demands consistent data to reach a sufficient confidence level. McConomy curves are such regression plots in use for rough estimation of sulfidation corrosion rates, as an integrated part of predicting overall high temperature refinery corrosion.[12] However, data on overall field corrosion rates consisting of naphthenic acid corrosion rates are highly scattered or exhibit a significantly high number of outliers.[13] Definition of appropriate evaluation metrics might seem a good way to bring scattered corrosion rate data together but it is difficult to define such parameters. In one such attempt, the empirical metric "sulfur/TAN ratio" was investigated pursuing the confluence of corrosion data but with limited success.[14] No other special metrics have been successful in evaluating naphthenic acid corrosion to the best of the authors' knowledge. Moreover, there is also a paucity of published laboratory corrosion data, especially comprehensive parametric studies. Therefore, a theoretical discussion has been presented here regarding a probable mechanistic pathway which can explain laboratory data on naphthenic acid corrosion.

MECHANISM OF NAPHTHENIC ACID CORROSION

The chemical equation for naphthenic acid corrosion of steel has been formulated as a redox reaction between iron and acids forming iron naphthenates and hydrogen as shown below.[15]

$$\text{Fe} + 2\text{RCOOH} \rightarrow \text{Fe(RCOO)}_2 + \text{H}_2 \tag{1}$$

Here, $R-$ is hydrocarbon moiety.

From a standpoint of physical chemistry, the above chemical reaction can be described as oxidative dissolution of metal but in non-electrolytic organic solution.[16] From common knowledge about similar other systems of oxidative dissolution, it can be inferred that the mechanism of naphthenic acid corrosion should involve transport of acids towards the steel surface, and redox reaction with steel followed by solvation (mixing/homogenizing) of iron naphthenates in the bulk hydrocarbon mixture.[16]

Among these steps, the rate of mass transport of acids towards the steel surface is computable as being proportional to concentration gradient of acids in the mass transport boundary layer.[17] However, molecular mass transport of acids is typically not the rate limiting step since the mass transfer coefficient is at least few orders of magnitude higher than the reaction rate constant in most cases. It is still important to calculate the rate of mass transport of acids in liquid phase for the calculation of near surface concentration of acids.

Elementary steps can be hypothesized for naphthenic acid corrosion reaction (1) by adopting the Lindemann-Hinshelwood approach, according to which the interaction of acids with steel should form an active intermediate Fe(RCOOH)*.[18–20] Such an active intermediate can be considered in the pseudo (quasi) steady state.[20] Further, surface active intermediate Fe(RCOOH)* reacts with another acid molecule to produce iron naphthenate which then dissolves in the bulk fluid mixture. The steps showing formation and further reaction of Fe(RCOOH)* are illustrated by Figure 1. The chemical reactions for the mechanism are given by (2) and (3).[20]

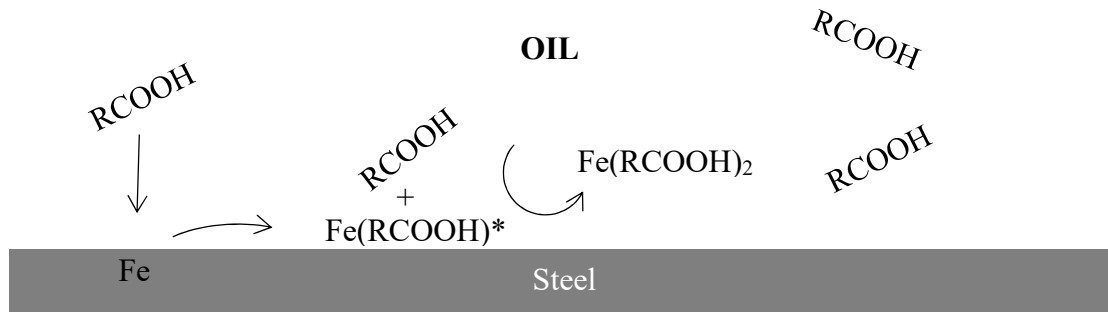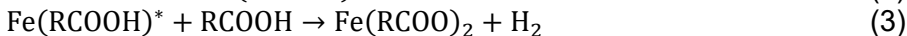**Figure 1: Proposed mechanism of oxidative dissolution of steel by naphthenic acids based on the Lindemann-Hinshelwood approach**

$$\text{Fe} + \text{RCOOH} \rightleftarrows \text{Fe(RCOOH)}^* \tag{2}$$
$$\text{Fe(RCOOH)}^* + \text{RCOOH} \rightarrow \text{Fe(RCOO)}_2 + \text{H}_2 \tag{3}$$

Now, the elementary reaction rate law for the first step, reversible reaction (2), can be written as follows.

$$r_{*(2)} = k_1 C - k_{-1} C_* \tag{4}$$

Here, $r=$ rate of formation/consumption of Fe(RCOOH)* for the particular reaction in mol·m^{-2}s^{-1}, subscripts indicate the equation number, $k_1 =$ rate constant for the forward reaction in m·s^{-1}, $C =$ concentration of RCOOH in bulk fluid in mol·m^{-3}, $k_{-1} =$ rate constant for the backward reaction in equation (2) in s^{-1}, $C_* =$ surface concentration of active intermediate Fe(RCOOH)* in mol·m^{-2}.

For the second step of the mechanism shown by reaction (3), the elementary rate equation can be written as follows.

$$r_{*(3)} = k_2 C C_*$$ (5)

Here, k_2 = rate constant for the reaction (4) in $m^3 s^{-1} mol^{-1}$.

A pseudo steady state hypothesis (PSSH) can now be applied for the net rate of formation of active intermediate Fe(RCOOH)*. According to this PSSH, the net rate of formation of the active intermediate is approximately zero.[20,21]

$$r_* = r_{*(2)} - r_{*(3)} = k_1 C - k_{-1} C_* - k_2 C C_* \approx 0$$

$$C_* = \frac{k_1 C}{k_{-1} + k_2 C}$$ (6)

Naphthenic acid corrosion rate can be considered as the rate of production of iron naphthenates. Substitution of C_* into equation (5) gives the rate law for calculation of naphthenic acid corrosion rate.

$$r_{*(3)} = r = \frac{k_1 k_2 C^2}{k_{-1} + k_2 C}$$ (7)

For the validation of equation (7), high temperature naphthenic acid corrosion experiments were performed on carbon steel specimens at a constant temperature of 343 °C for 24 hours, each test was conducted in a flow through mini autoclave (FTMA) reactor using a solution of a commercial naphthenic acid mixture in mineral oil. The design of the FTMA test apparatus can be found in a prior publication.[22] High temperature naphthenic acid dissolution rates for carbon steel samples are plotted *versus* different concentrations of the model naphthenic acid solution. The experimental corrosion rate data could be well fitted by equation (7) as shown in Figure 2.
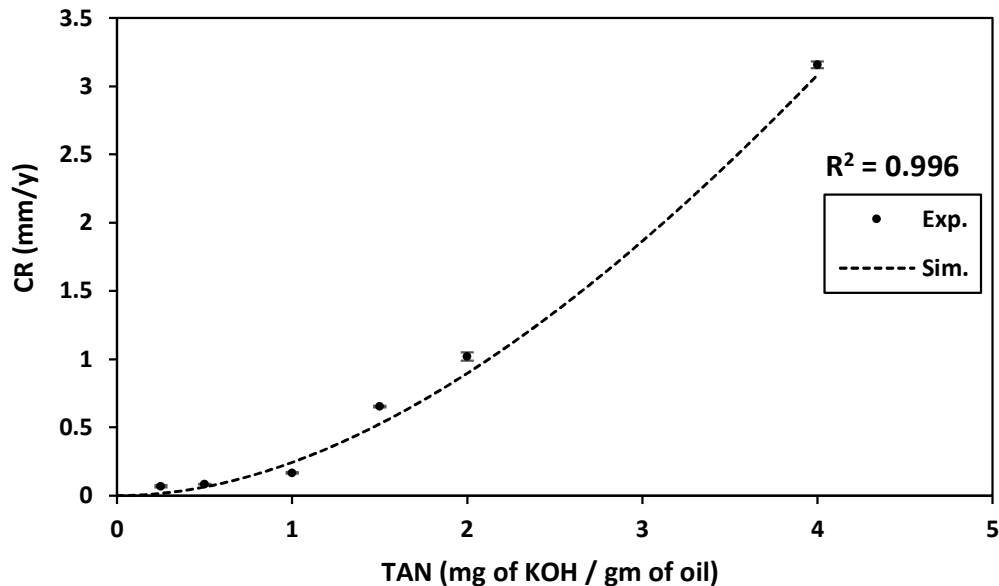

Figure 2: Experimental corrosion rates of carbon steel vs. concentration of acids fitted using equation (7). Carbon steel specimens were exposed to the solution of commercial model naphthenic acid mixture in mineral oil at 343 °C for 24 h in FTMA.

The reaction rate by equation (7) assumes an asymptotic trend with $r \to \infty$ for $C \to \infty$, which is also supported by the experimental data by Hau, *et al.,* explained further.[23] For not so different values of reaction rate constants k_1, k_2 and k_{-1} at given temperature, lower concentration of acids could also mean that $k_2 C \ll k_{-1}$. For this condition, corrosion rate should follow second order kinetics corollary to equation (7) as shown by equation (8) below.

$$r \approx \frac{k_1 k_2}{k_{-1}} C^2 = k_{eff} C^2 \tag{8}$$

Higher concentration of acids could mean $k_2 C \gg k_{-1}$, for which the corrosion rate follows first order kinetics as shown by equation (9).

$$r \approx k_1 C \tag{9}$$

Such a change in order of reaction kinetics from second order to first with increasing concentration was experimentally observed by Hau, *et al.,* in their "iron powder test", although the temperatures for the maximum dissolved Fe concentrations were different.[23] It should be noted that such a change in order of reaction kinetics is gradual and there is no exact transition point, but a "transition zone" which would depend on reaction dynamics. For the variety of naphthenic acid molecules in crude oil, the same Lindemann-Hinshelwood approach can be followed to derive reaction rate laws for the formation of homo- and hetero- iron naphthenates.

In most laboratory experiments the corrosion rate of carbon steel solely by organic acids increases linearly with their concentration up to indefinitely high values, resembling first order kinetics as depicted by equation (9).[1,3,8,24,25] This behavior is not exclusive to any particular type of molecular structure of acids.[1,3,8,24,25] The same behavior can be observed even for high temperature corrosion of carbon steel by fatty acids which are commonly found in high concentrations in biofuels.[1] The condition of $k_2 C \gg k_{-1}$ is required to be fulfilled to observe first order kinetics, $r = k_1 C$, as explained earlier. One may notice that $k_2 C \gg k_{-1}$ can be approached by either increasing concentration or by having $k_2 \gg k_{-1}$. The latter can arise due to inherent reaction dynamics, and it is not discussed in this paper. However, it can be observed from laboratory corrosion data that the condition of $k_2 C \gg k_{-1}$ is fulfilled if concentration and velocity of molecules are "sufficiently" high. Experimental corrosion data with high velocity of model oil solution of naphthenic acids is shown further as an example of first order kinetics. In the high temperature stirred autoclave, called high velocity rig (HVR), ring shaped specimens of carbon steel were installed around cylindrical rotor, and the test solution of model naphthenic acid mix with mineral oil was continuously passed through the chamber at the rate of 7-8 milliliters per minute at 343 °C. Effect of turbulent flow on mass transfer coefficient was replicated experimentally by rotating samples at 2000 rpm. The schematics of this apparatus have already been published elsewhere.[10] The corrosion rate increased linearly with the concentration of acids resembling first order kinetics given by equation (9) as illustrated by Figure 3.[26]
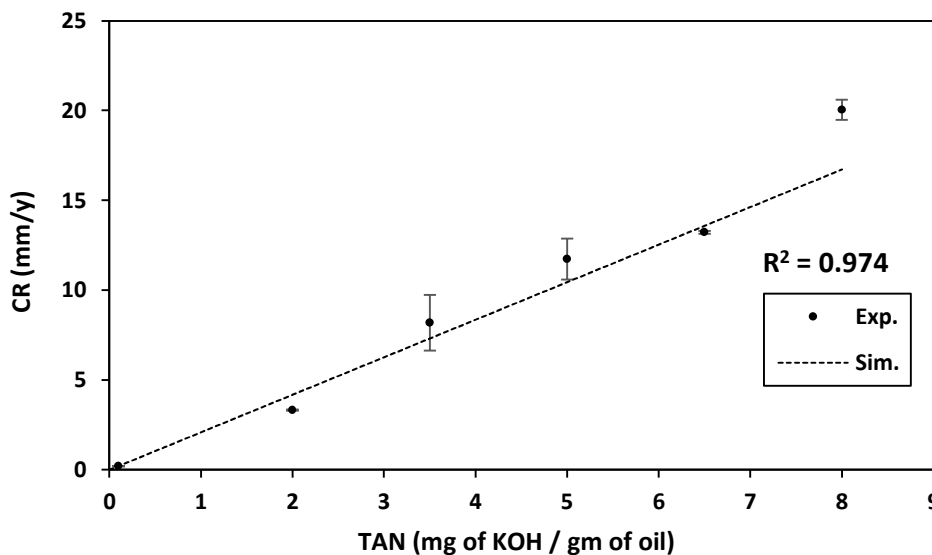
Figure 3: Corrosion rates of carbon steel vs. concentration of acids fitted using equation (9) for first order kinetics. Carbon steel samples were exposed to the solution of commercial model naphthenic acid mixture in mineral oil at 343 °C for 24 h in high velocity rig (HVR).[26]

The temperature dependence of reaction rate constant k_1 can be assessed by plotting the experimentally determined values in an Arrhenius plot as illustrated in Figure 4. These experiments were conducted by P. Jin in FTMA for 24 hours using model oil solution of TAN 3.5 by the naphthenic acid mix at the temperatures of 288, 316 and 343 °C, respectively. Higher concentration ensured first order kinetics at test temperatures. The activation energy determined from this plot was 46.5 kJ/mol. Moreover, the model naphthenic acid mixture contains numerous types of molecular structures of naphthenic acids. Hence, the activation energy value determined by this experiment is an average representative value for the mixture of acid molecules.
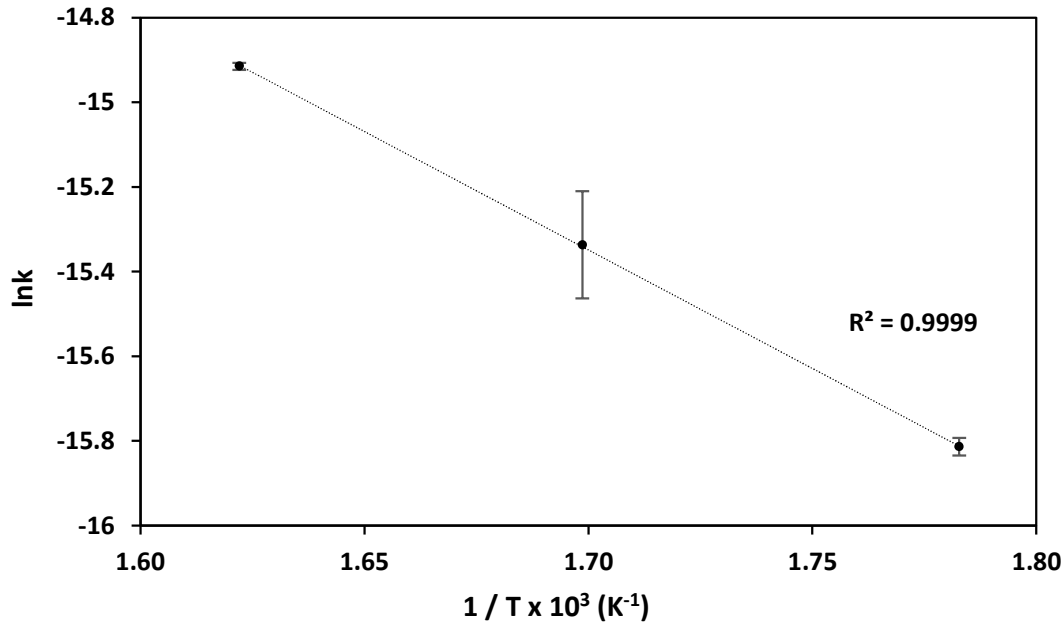

Figure 4: Logarithmic rate constant vs. inverse of absolute temperature for first order kinetics. Carbon steel samples were exposed to the solution of commercial model naphthenic acid mixture in mineral oil in FTMA. (Data source: Jin, 2018)[27]

It should be noted that a solid iron oxide layer is usually present on the steel surface during naphthenic acid corrosion.[10,11,28,29] The currently accepted mechanism for the formation of iron oxide is based on the thermal decomposition of iron naphthenates on the steel surface as shown by equation (10)**Error! Reference source not found.**.[10,11]

$$Fe(RCOO)_{2\,(oil)} \rightarrow FeO_{(s)} + RCOR_{(oil)} + CO_{2(g)}$$
(10)
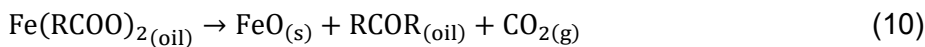
Iron oxide ultimately converts to non-stoichiometric Fe_3O_4 and in some cases to Fe_2O_3. To the best of the authors' knowledge, this mechanism has only been stated a few times in the literature as a hypothesis.[28,30] Additional literature is available on the synthesis of nano Fe_3O_4 particles of desired shape and size by thermal decomposition of Fe (III) carboxylates in a hydrocarbon matrix.[31–34] However, there was no mention in this literature about use of Fe (II) carboxylates which are of our interest. This mechanism was derived by considering the presence of ketones in solution as a proof of process occurring by the pathway shown by equation (10). However, the catalytic conversion of naphthenic acids in the presence of Fe_3O_4 also produces ketones as shown below, which is a commonly observed phenomenon.[7,35]

$$RCOOH + R'COOH \xrightarrow{-CO_2, -H_2O} R'COR \qquad (11)$$

If reactions (1) and (10) occur in a series, with higher concentration of naphthenic acids, higher quantity of the iron oxide must be produced and offer some sort of protection against further corrosion. However, no such effects are seen experimentally, rather, continuously increasing corrosion rates are observed with respect to increase in the concentration of naphthenic acids.[3,8] Also, magnetite has been shown to dissolve akin to iron by carboxylic acids.[7] Therefore, the mechanism of iron oxide formation by thermal decomposition of iron naphthenates shown by equation (10) cannot be settled unequivocally as of yet. It can be inferred considering the fate of the activated complex $Fe(RCOOH)^*$ that it can naturally decay further into other by-products in parallel to its reaction with bulk acid molecules. It can be hypothesized that $Fe(RCOOH)^*$ decays into iron oxide and aldehydes as shown by equation (10). This reaction was not considered in the previous treatment to maintain descriptive simplicity. However, the trend of the naphthenic acid corrosion rate with respect to concentration of acids do not change by addition of this parallel mechanism of iron oxide formation as it will be discussed further paragraphs. Iron oxide formation reaction can be written as below.

$$Fe(RCOOH)^* \rightarrow FeO + RCHO \qquad (12)$$

Elementary rate reaction for reaction (12) can be written as follows.

$$r_{*(12)} = k_3 C_* \qquad (13)$$

Here, k_3 = rate constant for the reaction (13) in s^{-1}.

By applying PSSH to the net rate of formation of active intermediate for both naphthenic acid corrosion by reactions (2) and (3), and iron oxide formation by reaction (12) we get total reaction rate as follows.

$$r_* = r_{*(2)} - r_{*(3)} - r_{*(12)} = k_1 C - k_{-1} C_* - k_2 C C_* - k_3 C_* \approx 0$$
$$C_* = \frac{k_1 C}{k_{-1} + k_3 + k_2 C} \qquad (14)$$

Substitution of this expression of C_* into equation (5) gives the rate law for calculation of naphthenic acid corrosion rate.

$$r_{*(3)} = r = \frac{k_1 k_2 C^2}{k_{-1} + k_3 + k_2 C} \qquad (15)$$

It is noteworthy from equation (13) the decay reaction (10) does not seem to affect the order of the kinetics of naphthenic acid corrosion, since the adoption of the same approximations $k_2 C \gg k_{-1}$ and $k_2 C \gg k_3$ lead to the first order kinetics for iron dissolution reaction; which is commonly observed experimentally even though iron oxide has formed. This is supported by experimental observations that iron oxide is formed in almost every experiment in small quantity but never seems to significantly change the trends in dissolution kinetics. Substitution of equation (14) into equation (13) gives the rate expression for formation of iron oxide. Due to the limitations of current instrumentation capabilities for the *in situ* chemical analysis of fluid mixtures in the reaction chamber at high temperature and pressure, it is not trivial to test the hypothesis for the formation of iron oxide by reaction (12).

CONCLUSIONS

High temperature naphthenic acid corrosion of carbon steel is hypothesized to proceed via an active intermediate which can be approximated to be in a pseudo steady state. The proposed mechanism attempts to correlate commonly observed first order kinetics for steel dissolution by acids in high temperature laboratory corrosion tests. A pathway for the formation of iron oxide during naphthenic acid

corrosion is proposed to be a consequence of natural decay of active intermediate. Further laboratory experiments need to be designed and performed to elucidate the mechanism for iron oxide formation.

ACKNOWLEDGEMENTS

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