

# Dynamic measurements of corrosion rates at high temperatures in high electrical resistivity media



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## ABSTRACT

A gallium orthophosphate crystal microbalance makes possible rapid measurements of dynamic corrosion rates at high temperatures in high electrical resistivity media. The crystal microbalance has allowed for the first time the determination of time resolved corrosion rates of iron immersed in an electrically insulating oil with naphthenic acid at high temperature (270 °C).

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## 1. Introduction

Discovering and confirming mechanisms of chemical reactions often depends crucially on the ability to measure reaction kinetics. The absence of techniques that measure the kinetics of corrosion of metals and metallic alloys directly at high temperatures (i.e., above about 100 °C) in environments of high electrical resistivity has limited our understanding of the mechanisms of corrosion in practically important media such as oil. For example, naphthenic acid corrosion in oil refineries typically occurs at temperatures in the range of 220–400 °C [1,2]. Because of the extraordinarily high electrical resistivity of the desalted crude that enters a refinery (similar to the electrical resistivity of mineral oil, which is  $\sim 10^{13-16}$  ohm-cm) electrochemical techniques, which are widely employed in measuring the rates of corrosion in aqueous and non-aqueous electrolytes, cannot be used [3]. Generally measurements of the kinetics of corrosion reactions in crude oil are limited to measurements of the average changes in weights of samples in tests conducted over times of at least several hours in duration and sometimes days and weeks [1,4]. Drastically increasing the sample's surface area by using fine powder samples has helped reduce the duration of the test [5,6]. However, there is a significant problem with conducting tests longer than just a few hours in crudes that contain naphthenic acids [7]. Naphthenic acids can decompose at high temperatures (e.g., 275 °C) so that the corrosiveness of the solution decreases with time [7]. The diminishing corrosiveness with increasing time makes it difficult to determine the true time-

dependency of a metal's corrosion rate. Even if acid-decomposition did not occur, measurements of average corrosion rates over relatively long periods of time are not as effective at discerning mechanisms of corrosion as are measurements of reaction rates as functions of time.

In this article we report the use of a gallium orthophosphate crystal microbalance to measure for the first time the corrosion rate of a metal as a function of time at high temperature in extremely high electrical resistivity media. Specifically, we report the measurement of the corrosion rate of iron as a function of time at 270 °C in mineral oil with 3 wt.% naphthenic acid ( $4 \times 10^{15}$  ohm-cm at 25 °C [8]).

Quartz crystal microbalances (QCM) have long been used to measure the dynamic mass changes in a variety of media at temperatures below 100 °C [9]. Unfortunately, the use of traditional quartz resonators (AT-cut) is difficult at temperatures above about 100 °C because the resonance frequency of common quartz crystals increases sharply with increasing temperatures above 100 °C [10]. Consequently, minor variations in temperature during testing cause greater shifts in the crystal's resonance frequency than shifts due to corrosion-induced changes in mass of the corrosion sample attached to the quartz crystal.

Gallium orthophosphate is structurally isotypic with quartz and exhibits a strong piezoelectric effect [11]. Fortunately, the temperature dependency of the piezoelectric resonance frequency of gallium orthophosphate can be tuned to operate optimally at temperatures ranging from room temperature to approximately 750 °C, and has been successfully implemented for measuring depositions at temperatures of up to 600 °C [12,13]. In principle, gallium orthophosphate can be employed in a crystal microbalance

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for measuring corrosion rates at temperatures as high as 970 °C [14].

## 2. Experimental

All chemicals were obtained from commercial sources. Naphthenic acid (Sigma–Aldrich) and RLOP base oil (Chevron ETC) were used to make the lab-simulated crudes. A cool drawer crystal holder (Inficon) was used with a custom-built 316 stainless steel autoclave for data acquisition. The autoclave contains two chambers, an upper chamber for preheating the oil, and a test chamber that contains the sample housed in the sample holder. The two-chamber device allows corrosion to commence at the high temperature of interest and allows data acquisition to occur almost from the instant the heated sample is first exposed to the hot oil-based solution.

5.8 MHz gallium orthophosphate crystal resonators with inbuilt gold electrodes were obtained from Piezocryst. The surface area of each electrode is 1.53 cm<sup>2</sup>. The resonance frequency of each crystal was 5.8 ± 0.1 MHz. Prior to deposition, crystals were ultrasonically cleaned in acetone and isopropanol to remove any surface contaminants. All samples were prepared using vacuum deposition techniques to maximize uniformity and minimize oxidation of the samples during their deposition.

Iron was deposited in a Perkins Elmer Randex RF sputtering system and the target purity was greater than 99.9%. The base pressure for all depositions was less than 9 × 10<sup>-6</sup> torr. Sputter deposition was performed using a shadow-mask to hold the crystals and control the sample area to 0.87 cm<sup>2</sup>. Samples of two micron (μm) thickness were deposited at a rate of 17 nm/min and were carried out with 175 W of power and 5 m torr of Ar. The thickness was confirmed via contact profilometry in an Alpha-Step IQ Surface Profile (KLA Tencor). Crystallinity of the sample was confirmed by XRD measurements using a PANalytical X'pert Pro diffractometer with an X'cellerator detector and a cobalt K<sub>α</sub> X-ray source.

In preparation for each corrosion test, a 450 mL volume of 3 wt.% naphthenic in oil was deaerated in a gas wash bottle (Ace Glass) by bubbling with house nitrogen at 80 °C for at least 4 h. While the solution was deaerating, an iron sample, which consisted of a 2 μm thick film of iron deposited onto a gallium phosphate crystal resonator, was placed into the microbalance's sensor head, and the sensor head was sealed to the autoclave using a compressible graphite gasket (McMaster–Carr). After sealing the autoclave, the system was flushed with nitrogen for five minutes at a very high

flow rate. A hand vacuum pump (McMaster Carr) was then used to transfer the oil from the gas wash bottle into the preheating chamber. After transferring the oil into the preheating chamber, the autoclave was brought up to the testing temperature (270 °C). After thermal equilibration of the two chambers, the valve to the test chamber was opened, and oil was transferred from the preheating chamber into the test chamber using nitrogen gas back-pressure to assist the transfer. After the transfer was completed, the crystal capacitance was tuned using the QCM controller (Maxtek), and data acquisition at a rate of 300 points/min was begun.

A schematic of the autoclave is shown in Fig. 1. After data acquisition was completed, pressurized nitrogen gas was used to remove as much oil from the sample chamber as possible, and the autoclave was cooled to room temperature. After cooling to room temperature, the sample was removed and sonicated in hexane to remove any residual oil. Surfaces of corrosion-tested samples were investigated with a 5 kV–12 μA electron beam in a JEOL Field emission scanning electron microscope equipped with an EDAX Energy-Dispersive Spectroscopy (EDS) system and a backscatter detector. Samples were electrically grounded with carbon tape to prevent charging.

## 3. Results and discussion

A crystal microbalance is sensitive to several effects that affect its resonance frequency, including mass loading, thermal frequency shifts, liquid–electrode viscosity loading, as well as other factors that are usually less significant (including pressure and surface roughness). The factors that contribute to shifts in the resonance frequency are summarized in the following expression.

$$\Delta f = \Delta f_{mass} + \Delta f_{thermal} + \Delta f_{viscosity} + \Delta f_{other} \quad (1)$$

Gallium orthophosphate crystal microbalance (GPCM) mass loading was calculated using the method of Lu and Lewis, which is a variation of the Sauerbrey equation that accounts for viscoelasticity differences between the thin film sample and the piezoelectric crystal [15]. To obtain the mass loading on the crystal, the following relationship presented in Eq. (2) was applied.

$$\Delta m = -\tan^{-1} \left( \tan \left( \frac{\Delta f \pi}{f_o} \right) \frac{Z_{GAPO}}{Z_{Fe}} \right) \frac{Z_{Fe}}{2\pi f} \quad (2)$$

$f_o$  is the fundamental frequency (Hz),  $\Delta f$  is the change in frequency (Hz),  $Z_{GAPO}$  is the acoustic impedance of gallium orthophosphate

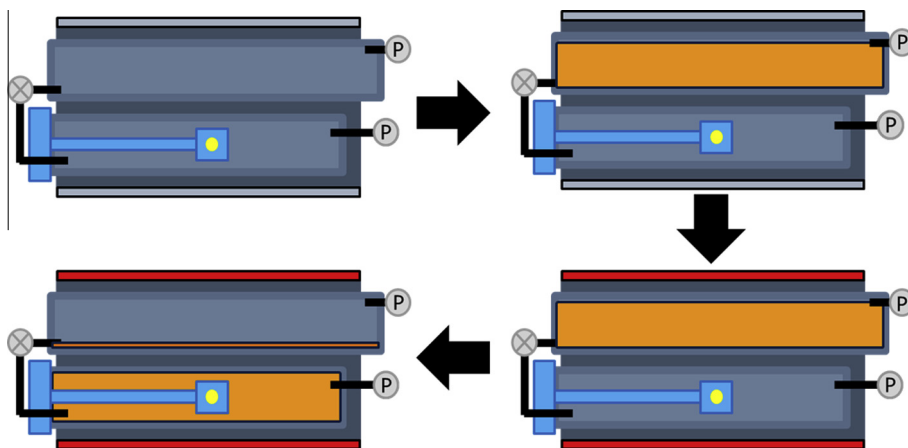


Fig. 1. Schematic of stainless steel autoclave and procedure of preheating oil-based solution and transferring solution into sample's test chamber. Clockwise from the upper left: Microbalance sample positioned in the sample chamber; filling of oil-based solution into the pre-heat chamber, which is located above the test chamber; heating of the oil-based solution and of the test chamber; transfer of oil-based solution into the test chamber once the pre-heat and test chambers have reached thermal equilibrium.

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