

Demonstration of a New Direct Corrosivity Sensing Method for Fast Evaluation of Inhibitors . The μ Coupon concept

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Abstract

A new direct corrosivity sensing method is investigated for rapid checking of the effectiveness of inhibitors and inhibitor compositions on corrosion of ferromagnetic materials in fluids. The sensor is based on the application of continuous measurement of the inductivity of a small flow-through solenoid structure with a miniaturized ferromagnetic coupon (μ Coupon) in its core which contacts the flowing corrosive fluid. The μ Coupon sensor is constructed by applying 1–2 mg fine powder of the ferromagnetic metal on a nonmetal surface

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using an external static magnetic field across the solenoid as immobilizing tool. Application of the fine-powder-coupon is a factor of the corrosion acceleration which allows a fast and reproducible testing of the corrosion rate of the coupon-material in the sample solution. The inductivity value is in linear correlation with the ferromagnetic mass in the coupon, therefore the system provides continuous reading of the mass corrosion rate value within the life of the coupon material. In the corrosion rate measurement ~ 140 ng Fe/min is the estimated detection limit of the present construction of the μ Coupon sensor. The magnetic susceptibility value is not affected by the interfacial chemistry of the metal particles and insensitive to any nonmagnetic deposits. With this approach the μ Coupon technique provides a real-time fluid corrosivity sensing and it is totally independent of composition of the fluid phase and of the inhibitor. We demonstrate the operation capability of the method in aqueous phase by showing the effect of 1-hydroxyethan-1,1-di-phosphonic acid (HEDP) containing protecting additive on the acidic corrosion of Fe. In the laboratory test a tap water based test solution is pumped from a stirred vessel through a solenoid cell of 0.5 mL volume. An accelerated test requires only 1 hour to evaluate the effectiveness of a corrosion inhibitor added to the test solution.

Keywords: corrosivity test, inhibitor efficiency

Introduction

Here we summarize the main measurement approaches used in corrosion investigation practice.

Mass sensing methods

The well known and widely used coupon technique utilises macro-sized probe and it is capable only to provide cumulative corrosion data over long periods, however, there is the possibility to characterize the corrosion process. Due to their physical size, macro-coupons behave

in a physically similar way to the parts in the real technological processes. Screening of the effectiveness of different inhibitor compositions through this method is a tedious work.

The quartz crystal microbalance (QCM) and similar techniques (surface acoustic wave SAW, Micro-electromechanical sensor MEMS, cantilever oscillation) are inherently applicable to study the corrosion process in the real-time measurement of the mass-time function on a film made from the investigated material. These devices are readily applicable for gas corrosion detection since their operation is almost ideal in a medium where the low viscosity allows the range of $10^{-8} - 10^{-9}$ g mass change sensitivity. [#ref01], [#ref02].

In solution phase, due to the much higher fluidum viscosity, the mass change sensitivity of QCM is significantly less, only $10^{-6} - 10^{-7}$ g. However, QCM received extensive application in electrochemical investigations (Electrochemical QCM, EQCM) including studies on the corrosion process. For detailed investigation of thiazole-type inhibitors for acidic sulphate corrosion of Cu (a simple process without film deposition) was possible by QCM and separated AFM and EIS investigations [#ref03]. In this work the rate of the copper mass change due to dissolution was on-line recorded for 20000 sec at different solution compositions.

Studying chromatation of Zn it was clearly concluded that QCM alone can not provide unambiguous information on the corrosion since the total mass changing is a balance of dissolution and different film precipitations, therefore requires additional techniques to deconvolute the overlapping processes. [#ref04]

Generally, the real-time initial mass sensing methods are not selective for the metal loss which is, per definitionem, the fundamental phenomenon of the corrosion.

Electrochemical sensor principles

These methods are based on well established correlations to the theoretical corrosion processes which are electrochemical in nature. Unfortunately, the electrochemical sensors are very sensitive for interface charge transfer processes, suffer from many interferences caused by the fluidum compositions, and they are very much depending on the precleaning of the sensor surface.

Magnetic methods

When a constant magnetic field is applied together with a magneto-color 'pigment' painting that transposes surface distribution of B field into color-contours, a 2-dimension corrosion map can be generated in case of ferromagnetic materials. Its special advantage is the direct photo documentation of relatively large investigation area (100–1000 cm²).

Alternating magnetic field generates eddy current in conductive materials. Its magnitude greatly depends on the continuity of the conductive material and the distance measured from the sensor. It means that presence of homogeneous, thin film-like layer can be detected. Corrosion ruins the uniformity of the conductive layer, hence it hinders the generation of eddy current. A unique advantage of this technique that hidden corrosion for instance under paint layers can also be successfully detected by it.

The μ Coupon concept

The proposed method is designed to fill the gap between the electrochemical sensors (fast response, excellent time resolution, oversensitive nature to interferences) and the classic coupon technique (extremely slow response, no time resolution) by using a probe made of ferromagnetic metal particles (total particle mass is in the mg range) and recording the mass loss through measurement of the magnetic susceptibility value.

This technique is based on the absolute ferromagnetic mass signal, therefore it is a new approach for fast corrosivity testing. According to the sensing principle this technique can provide a chemical interference free and realtime tracking of the corrosion rate of ferromagnetic materials in any type of fluidums like aqueous solutions, oils and other organic fluids, gases like ambient air, exhaust fumes and technological gas streams.

The volumetric magnetic susceptibility is the dimensionless proportionality factor of the magnetization of a material in H magnetic field:

$$\mathbf{M} = \chi_v \mathbf{H} \quad \text{Eq. 1}$$

In Eq. 1, \mathbf{M} is the magnetization vector of the material (the magnetic dipole moment per unit volume), measured in $A \, m^{-1}$ and \mathbf{H} is the magnetic field strength vector, also measured in $A \, m^{-1}$. For ferromagnetic material, volume magnetic susceptibility χ_v is positive and is in the range of 100 – 100000. The magnetic induction \mathbf{B} is related to \mathbf{H} by Eq. 2. in which μ_0 is the magnetic constant and $(1 + \chi_v)$ is the dimensionless relative permeability of the material.

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = \mu_0 (1 + \chi_v) \mathbf{H} = \mu \mathbf{H} \quad \text{Eq. 2}$$

The magnetic susceptibility and the magnetic permeability are related by the following formula:

$$\mu_0 (1 + \chi_v) = \mu_0 \mu_r = \mu \quad \text{Eq. 3}$$

There are two other measures of susceptibility, the mass magnetic susceptibility χ_{mass} , measured in $m^3 \, kg^{-1}$ and the molar magnetic susceptibility (χ_{mol}) measured in $m^3 \, mol^{-1}$ that are defined below, where ρ is the density in $kg \, m^{-3}$ and M is molar mass in $kg \, mol^{-1}$.

$$\chi_{\text{mass}} = \chi_v \rho^{-1} \quad \text{Eq. 4}$$

$$\chi_{\text{mol}} = M \chi_{\text{mass}} = M \chi_v \rho^{-1} \quad \text{Eq. 5}$$

The inductance of a solenoid with a full size core (the total volume of the solenoid is filled with a homogeneous material) is given by Eq. 6, where L is the inductivity, in Henry (H), A is the cross section area in m^2 , and l is the solenoid length in meters.

$$L = \mu N^2 A l^{-1} \quad \text{Eq. 6}$$

In case of partial filling of the solenoid by a material, the total inductivity, L can be calculated by Eq. 7/a, where L_0 is the inductivity with air core, k is a factor depending on solenoid parameters, frequency, temperature, material distribution, material μ_r and ρ specific gravity, M is the magnetization of the material (the magnetic dipole moment per unit volume) and m is the mass of the material.

$$L = L_0 + k M m \quad \text{Eq. 7/a}$$

$$d(L - L_0)(dt)^{-1} = k M dm (dt)^{-1} \quad \text{Eq. 7/b}$$

In this case we suppose that the amount of the additional ferromagnetic material is negligible and total inductivity can be calculated by simple linear superposition. This means that the changing rate of inductivity is proportional to the ferromagnetic mass changing rate caused by the corrosion process, as presented in Eq. 7/b, which is the derivative of Eq. 7/a.

Using homogeneous, magnetically isotrope material, like metal powder, any kind of immobilisation inside the coil can be applied as long as some well-defined conditions are fulfilled. The whole amount of immobilised material must be inside the measuring coil, where the presence of homogeneous magnetic field is a good estimation.

The simplest way of calculating χ is the measurement of coil inductivity with and without the sample of unknown magnetic susceptibility being placed in the centre of it. Measured complex impedance of the coil equals to $2 \pi j \omega L + R$, where j is the imaginary constant unit. In the case that eddy current effect is not negligible, R

becomes a sum of the coil resistance and the iron loss resistance which is in the k_e factor of the eddy loss given by Eq. 8. To eliminate the possible cross-effect of the eddy current on inductivity measurement, we used sample of loose consistency such as iron powder.

$$P_e = k_e f^2 B_{\max}^2 \quad \text{Eq. 8}$$

As iron particles may also join together to provide paths to eddy currents, distribution of iron powder should be arranged in such topology that does not allow creating of electric contacts between them, has the smallest total cross section area perpendicularly to the axis of the coil and can not create a short circuit in the cross section. Such short circuit would result in a transformer with the measuring coil being the primary and the sample as the secondary coil shortened through its series resistance. Requirements of iron powder distribution were satisfied with magnetic immobilisation of hydrogen reduced iron powder used as the μ Coupon sample.

Measurement set-up

Fig. 1 shows the basic scheme of the structure of the μ Coupon sensor cell. A glass tube of 4 mm OD and 3 mm ID is the base of the solenoid which is made of 200 windings of \varnothing 0.06 mm Cu insulated wire.

1–5 mg fine ferromagnetic powder, the microcoupon material is magnetically immobilised onto the inner wall of the glass tube. Two immobilizing magnets are set diametrically onto the surface of the windings, whereas the arrangement generates a static field perpendicular to the solenoid axis. This static cross-field can be generated either by rare earth metal (REM) magnets or an electromagnetic circle. The last technique provides the possibility to switch off/on the immobilizing field through the solenoid, hence gives a controlling tool for changing/releasing the Fe powder content of the cell.

Measured inductance of the coil is observed to be in correlation with the ferromagnetic mass.

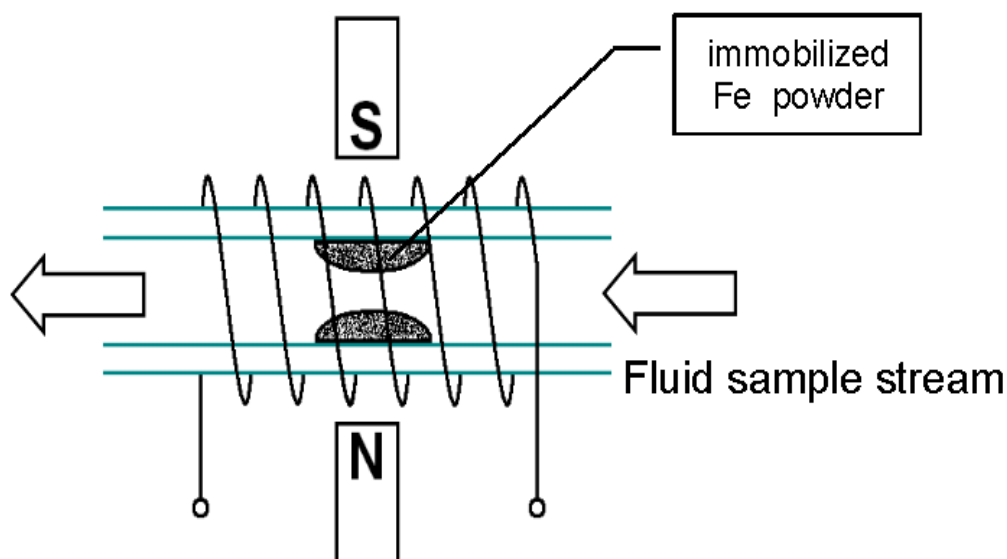


Fig. 1. The structure of the μ Coupon sensor cell. Solenoid with magnetically immobilized iron particles. S–N : orthogonal static magnetic field.

Inductivity of the coil is measured with a **HP 4284A** LCR measuring instrument. The instrument measures the absolute value of impedance and phase and can calculate series impedance and quality factor, if non-ideal inductivity model with series resistance is the model it is forced to calculate with.

First the empty coil was measured, this value is used as a reference, L_0 . Immobilised ferromagnetic material in the measuring coil increases inductivity, it can also be measured. This is the starting inductivity, L_{START} as it is referred later, $L_{\text{START}} - L_0$ is the value to which the measurements then normalised.

Generally, in aqueous environment, the iron corrosion causes the ferromagnetic mass to slowly convert into oxides and hydroxides. To avoid the interference of the development of magnetite composition, the acidic acceleration was applied. In this case the corrosion products do not modify coil inductance.

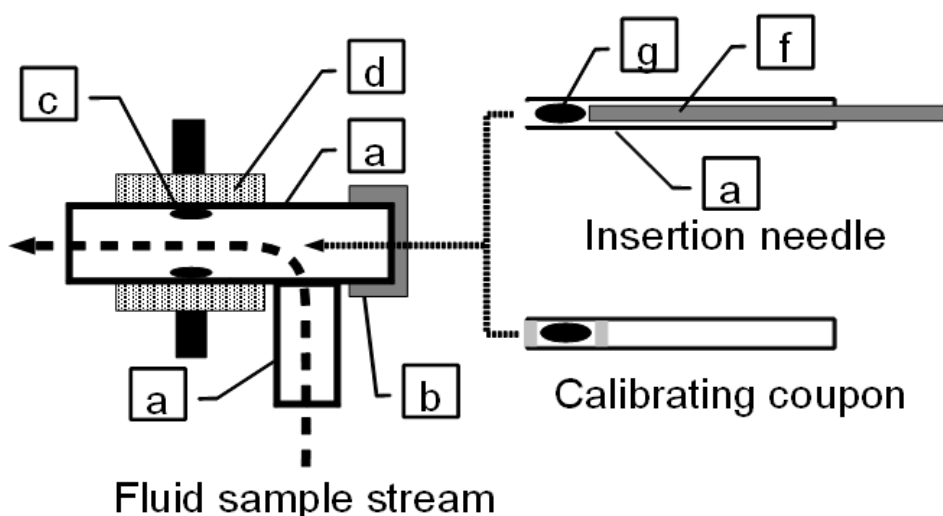


Fig. 2. Scheme of the μ Coupon cell with the insertion needle system for the Fe particles and the calibrating coupon

- a. T-piece for sample flow and insertion port
- b. Insertion port cup
- c. Immobilized Fe particles in the cell
- d. Solenoid winding and the rare metal magnet cubes
- e. PTFE insertion tube
- f. Cu wire-piston
- g. The Fe particles before insertion into the μ Coupon cell

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Calibration for Fe mass

The μ Coupon cell was calibrated in the 0–4 mg Fe mass range by making 5 individual calibrating needles with different Fe amount, including zero (Fig. 2). These needles were made of PE capillary by closing different amount of Fe powder between two silicone plugs at one end. The Fe mass was set by gravimetry before closing the capillary. Mass accuracy was 0.02 mg.

Each calibration needle was inserted to the centre of the solenoid and the inductivity was measured at different frequencies in the range of 0.2 – 600 kHz.

The inductivity vs. frequency function was investigated, a typical diagram is presented in Figure 3. Quality factor of the coil was also noted, as this value is necessary in deciding whether the eddy current loss was present in the measurement or not. Measuring frequency for corrosion rate test was chosen to be 1 kHz, near the flat top region of the characteristics. This choice caused less error in the measurements due to changes in excitation frequency.

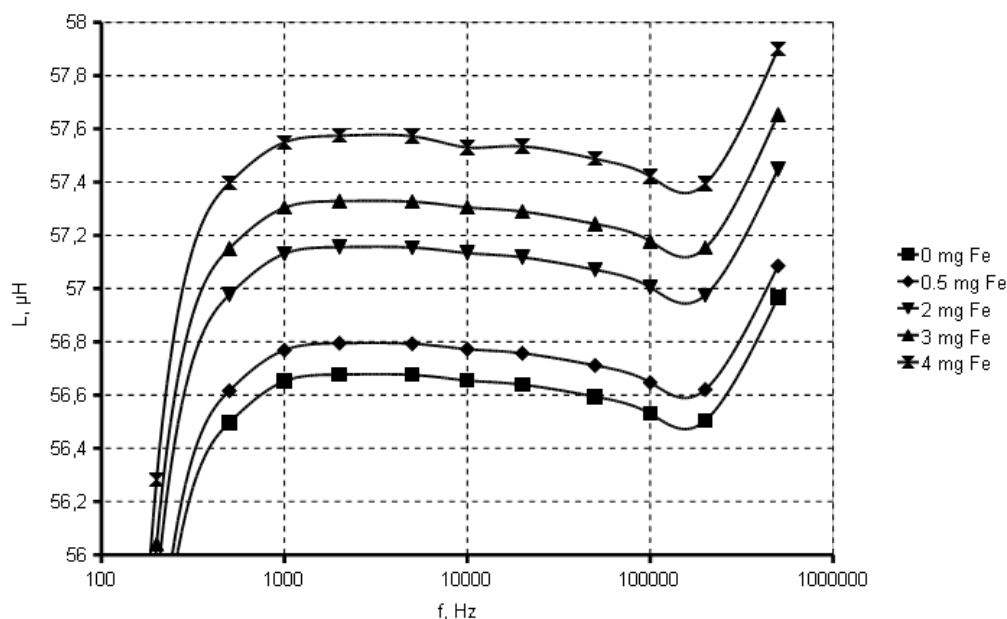


Fig. 3 Inductivity vs. frequency plot for the μ Coupon cell

Quality factor of a solenoid is a ratio of the pure inductance over the resistance component.

$$Q = |X_L (R_e + R_{cu})^{-1}| \quad \text{Eq. 9}$$

where X_L is the inductance which linearly increasing with the frequency, R_{cu} is the resistance of the copper wire winding, R_e is the equivalent resistance of the energy dissipation (Eq. 8) caused by the eddy currents in the core material (these latters are frequency independent).

Figure 4 shows a good linear function of quality factor which is proved to be independent of iron mass in the coupon. Even at 500 kHz, the iron mass present in the measuring coil does not cause considerable change in the quality factor and thus eddy current effects are negligible at the applied test parameters.

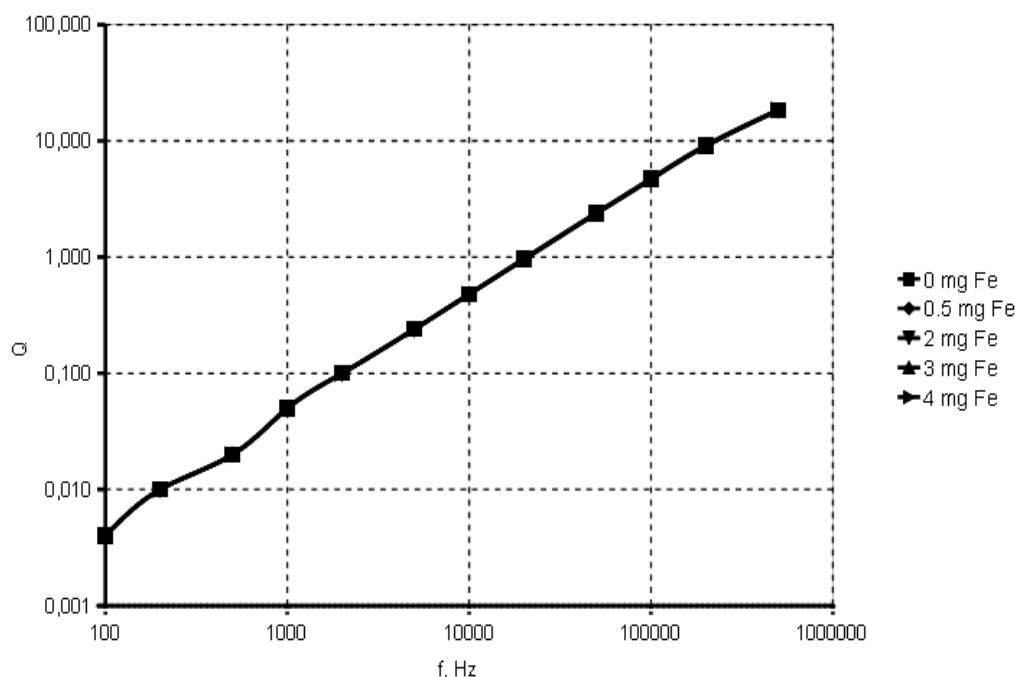


Fig. 4. Investigation of Fe mass on the quality factor of the μ Coupon cell

Correlation between ferromagnetic mass and coil inductance was examined to establish the calibration curve for mass sensing. Theoretically, when the air gap in the magnetic circuit is long enough, the absolute change in coil inductivity will be proportional to ferromagnetic mass inserted in the centre of the coil according to Eq.7/a. At the chosen frequency, however, this statement was investigated to prove linearity.

Results are presented in Fig. 5 for two different cases, with and without the outer static magnetic immobilising field according to the arrangement shown in Fig. 1.

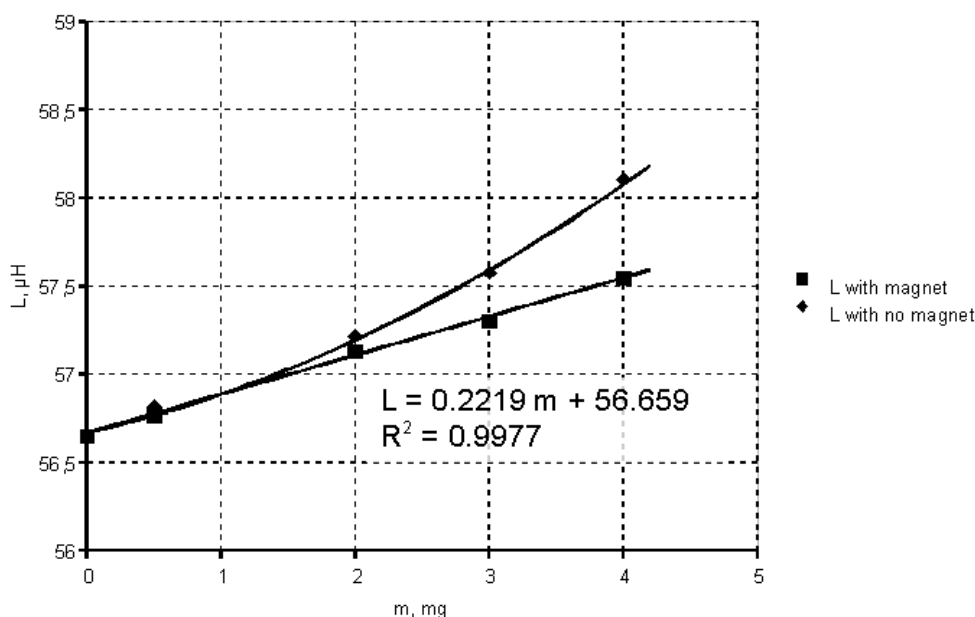


Fig. 5 Calibration plots of μ Coupon at 1000 Hz. Solid line: with outer static magnetic field, broken line: without static magnetic field

Result of calibration test shows that correlation between ferromagnetic mass and coil inductivity is linear when an orthogonal static magnetic field is applied. The regression line in this case has 222 nH/mg Fe slope which is the absolute mass sensitivity of the sensor system. This effect also indicates that the immobilising magnetic field is useful not only because its contactless nature of operation but the linearising effect upon ferromagnetic mass measurement. It means that the relative inductivity change rate is linearly proportional to mass change rate as shown earlier in Eq. 7/b.

To avoid the need of the tedious weighing preparation to set the same ferrous mass, m_0 for each coupon, the normalised corrosion rate (NCR) is defined as normalised ferromagnetic material mass decrease rate :

$$\text{NCR} = - \frac{dm}{m_0} (dt)^{-1} \quad \text{Eq. 10/a}$$

Its combination with Eq. 7/a and 7/b results in the following fundamental μ Coupon equation.

$$\text{NCR} = -d(L - L_0) (L_{\text{START}} - L_0)^{-1} (dt)^{-1} \quad \text{Eq. 10/b}$$

Where L_{START} is the inductivity recorded immediately after the insertion of the Fe powder through the needle system shown in Fig.1(e), L is the time dependent value and L_0 is the constant representing the sensor inductivity in case of non-ferromagnetic core (air or water).

This method provides well comparable NCR values of the different test runs having unweighed Fe powder amounts immobilized in the measuring cell.

Experimental

Materials

Fe powder: hydrogen reduced iron powder, particle size 0.05–0.1 mm, Ferrum Reductum p.a., manufacturer REANAL Budapest (Hungary)

Water: Budapest tap water (BTW) with average composition of COD 0.56 mg/l, Cl^- 22 mg/l, Fe 25.6 mg/l, Mn 3.5 mg/l, NO_3^- 9.0 mg/l, NO_2^- <0.03 mg/l, NH_4^+ < 0.04 mg/l, Total Hardness 143 mg/l CaO, Conductivity 475 $\mu\text{S}/\text{cm}$

Inhibitors:

- Corin PW-38T (consists of HEDP 12.2 w%, zinc sulphate- H_2O 9.55 w%, sulphuric acid 5 w%, Acumer 2000 scaling inhibitor 6 w%, Tolyltriazole 0.25 w%), manufacturer KEMOBIL Rt, Tatabánya (Hungary)
- HEDP: Cublen K60 (60 w% HEDP), manufacturer Zschimmer & Schwarz Mohsdorf GmbH (Germany), we prepared a HEDP reagent solution of 6 w% HEDP by 1:10 dilution of the manufacturers stock solution with deionized water.

Corrosion experiments

As shown in Fig. 6 the set-up of the corrosivity measurement is very simple. 1000 mL test solution made of BTW in a stirred baker is the examined fluid. This solution was pumped through the μ Coupon cell with 5 mL/min flow rate with a peristaltic pump.

Accelerated corrosion was generated by acidification of the test solution, while decreased corrosivity was achieved by adding corrosion inhibitor to the test solution.

Measurements were performed at ambient temperature after the whole system including the test solution and the microcoupon cell has reached its equilibrium temperature. This stabilisation was important because of the temperature-sensitivity of the coil inductivity. First L_0 value was measured, this value was subtracted later from every inductivity value to get the additive inductivity generated by ferromagnetic mass inserted into the coil.

The μ Coupon system requires to stop the water circulation while the ferromagnetic powder is immobilised into the measuring cell. This intermission takes about 4–5 seconds, and according to our observations it does not alter the signal level.

Corrosion of ferromagnetic material begins immediately when it contacts the test solution, hence immediate readout of L_{START} is important. This starting value of the inductivity is necessary for the measurement data to be normalised to.

Effects of the different compositions were observed through 15–20 minutes by reading the inductivity value in every minute. This amount of data is enough for calculation of time function slope of $L(t)$ and the corrosion rate.

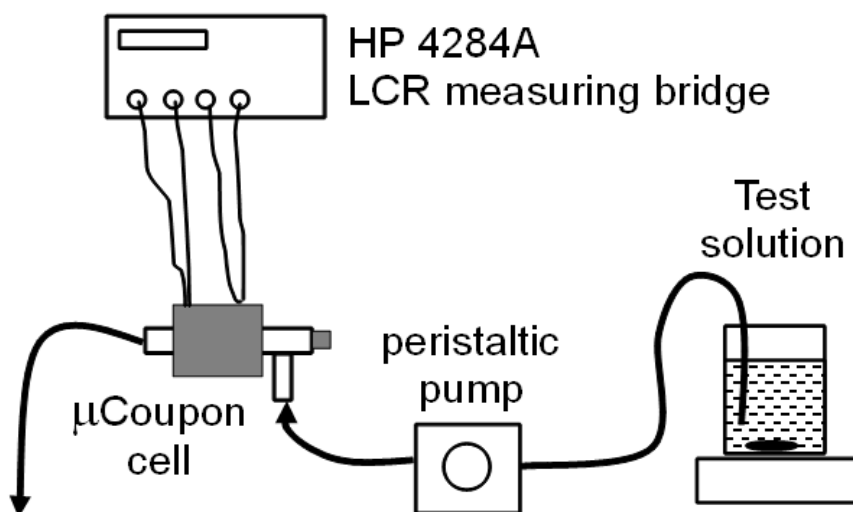


Fig. 6 Measuring set-up with flow-through fluid system

Raw measurement data recorded as a function of time include L_0 value, ferromagnetic $L(t)$ time function, both sensitive to changes of temperature and additive error (Fig. 7). We have observed rare inductivity value jumps with magnitude of 20–30 nH that persists for random duration in the range of 10–40 minutes. This signal jump comes from the operation stability of the measuring bridge, which is reported to be in this range.

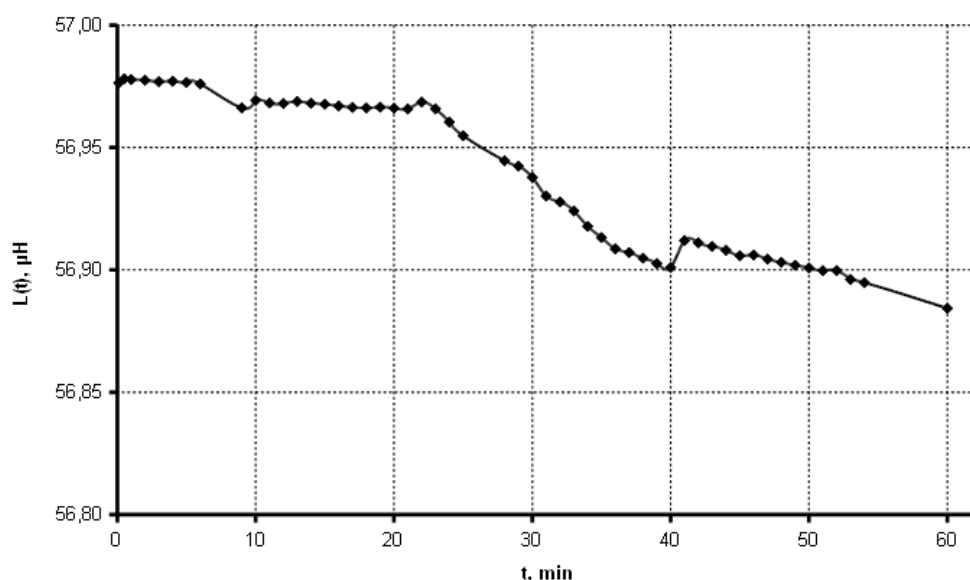


Fig. 7 Plot of raw measurement data

This kind of error can be easily compensated in the data treatment by an additive constant for the time period where the observed error persists.

Relative ferromagnetic mass is calculated from inductivity data points by subtracting L_0 value from them and dividing the difference by $L_{\text{START}} - L_0$. As it was stated earlier, normalised inductivity change is proportional to ferromagnetic material, slope of this normalised function is equal to the normalized corrosion rate of ferromagnetic mass according to Eq.10/b.

The normalised and jump-corrected time function of Fig. 7 is presented in Fig.8.

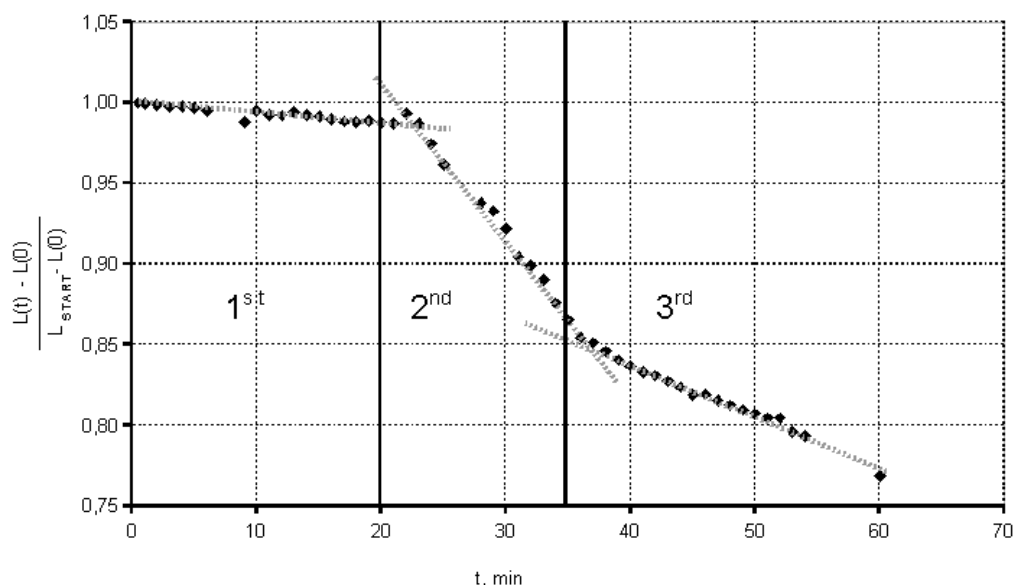


Fig. 8. Typical normalized plot of the μ Coupon testing of inhibition: relative Fe mass vs time

Experiments were carried out according to the following scheme. First period begins when ferromagnetic microcoupon material is immobilised inside the measuring cell, and neutral test solution flow starts. During this phase the neutral corrosion rate, as a background is measured for 20 minutes. In the second period proper amount of acid was added to the test solution to set pH 2.3–2.4 to enhance its corrosivity. Length of this accelerated phase was varied to allow both calculation of the iron mass decreasing rate and avoiding total iron loss of greater than a limit. We decided that total iron loss of 25% is the limit that should not be exceeded during the accelerated measurements. In the third phase, the investigated corrosion inhibitor was added to the test solution to decrease corrosion rate and to demonstrate the capability of the microcoupon sensor to examine corrosion inhibitor effectiveness. Inhibitor used here was Corin PW38T.

Corrosion rates were calculated from time function of relative inductivity change vs. time functions. We assumed these functions to

be equivalent to ferromagnetic iron mass vs. time functions. By fitting linear functions to these data points corrosion rate can be derived as given in Equation 10/b. In the experiment presented in Figure 8, the normalized corrosion rates were the followings values.

1st section – corrosion in neutral water (BTW):

$$\text{NCR}_1 = 0.06 \% / \text{min.}$$

In the 2nd section, after setting the pH of the test solution to pH 2.4 by adding 1:1 HNO₃ to it, the corrosion rate is

$$\text{NCR}_2 = 0.94 \% / \text{min.}$$

In the 3rd section an addition of 200 µl of PW38T decreased the corrosion rate to

$$\text{NCR}_3 = 0.32 \% / \text{min}$$

Corrosion inhibitor efficiency (CIE) was calculated with the following relationship:

$$\text{CIE (\%)} = 100 (\text{NCR}_2 - \text{NCR}_3) / \text{NCR}_2 \quad \text{Eq. 11}$$

In the presented experiment the inhibitor efficiency of PW38T in acidic corrosion of Fe (powder) in tap water at pH 2.4 was 66%.

Estimation of the detection limit in the accelerated corrosion

Upon the signal to noise ratio seen in the 1st section of the plot in Fig. 8 the detection limit of the mass decreasing rate is approximately – 0.01% /min, that is 1/6 of the observed NCR in the neutral solution phase. Using the $L_{\text{START}} - L_0$ value, the calibration plot in Fig. 5 returns the actual m_0 of 1.4 mg Fe in the coupon for this experiment.

It is then calculated from the above data that $10^{-4} m_0 \sim 140 \text{ ng Fe} / \text{min}$ corrosion rate is the detection limit of the present construction of the

μ Coupon sensor. This is in the same sensitivity range than that of the EQCM method.

Inhibition study on synergic effect with HEDP and ZnSO_4 (PW38T)

The sensitivity of the μ Coupon technique provides the possibility to investigate the combined effects of inhibitor molecule and different additives. In this preliminary work we demonstrate the HEDP and Zn ion synergic inhibition effect on the Fe corrosion.

The first group of the test runs were made by adding different amounts of Corin PW38T inhibitor composition to the test water at the 35th minute, according to the technique shown in Fig. 8. Using value of 150 g HEDP / litre in the PW38T stock solution, the HEDP equivalent value of each the addition was calculated.

Inhibition efficiency values of Eq. 11 revealed a threshold concentration at 75–90 ppm with a top efficiency of 70–75%. As the $\text{ZnSO}_4 \cdot 2 \text{H}_2\text{O}$ content of the PW38T is 9.55 w%, this curve represents the combined inhibition effect of a HEDP– Zn^{2+} composition.

To evaluate synergic effect of Zn ions a stock solution of pure HEDP acid was used with 1:10 dilution of the Cublen K60 containing 6 w% HEDP. In this case the HEDP concentration values in the test solution were set to the same values as those applied in the previous experimental group. The synergic effect of Zn and HEDP is clearly seen in Fig. 9.

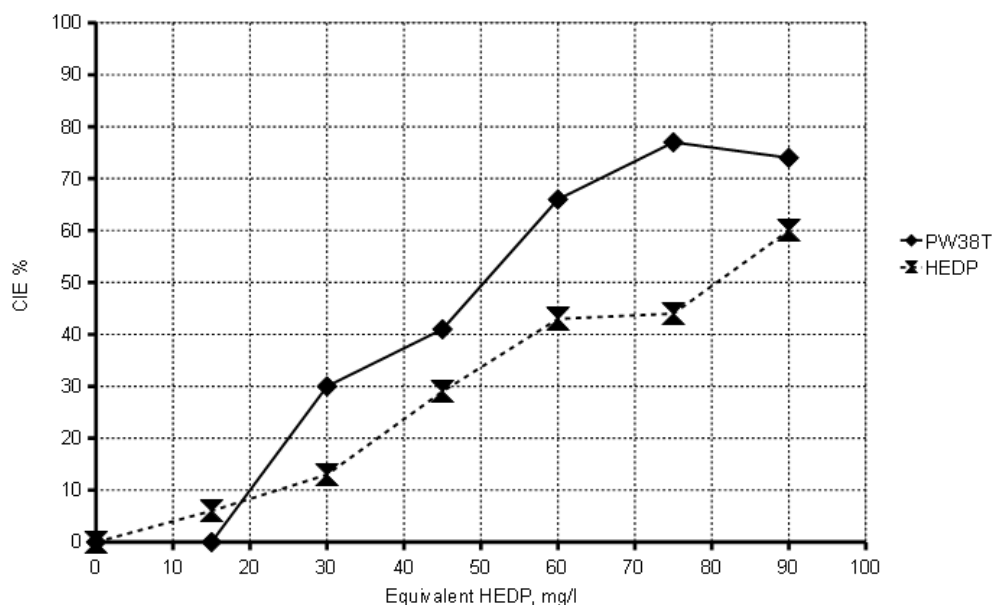


Fig. 9 Inhibition study on Fe with PW38T composition and with HEDP against acid corrosion in water at pH = 2.4

Conclusion

As shown above the μ Coupon technique offers fast and objective evaluation of inhibitor efficiency on accelerated Fe corrosion within a 1 hour experimental run. In this way it is possible to screen potential inhibitor compounds and synergic effects by comparing the efficiency plots similar to that shown in Fig 9.

Further investigations will cover wide selection of different inhibitors and compositions, temperature as well as salt effects.

Further development of the method to achieve a more standardized technique is in progress.

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