

## **Accuracy and Validation of Corrosion Rates Measured by the Tafel Method in H<sub>2</sub>SO<sub>4</sub> Solutions**

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## Abstract

Accuracy and validity of the Tafel extrapolation method for determining corrosion rates of carbon steel in 1,2 and 3N H<sub>2</sub>SO<sub>4</sub> solutions open to air is discussed. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests were performed employing three different working electrode pre-treatments. Comparison of data obtained from Tafel extrapolation and EIS indicated that these two methods are in good agreement. For confirmation, corrosion rates obtained from Tafel extrapolation were compared with weight loss (WL) method. It was shown that most corrosion rates obtained from Tafel method were much larger than that of WL method.

**Keywords:** 'Carbon steel, EIS, Potentiodynamic polarization, Tafel method, Weight loss'

## 1. Introduction

With respect to the determination of corrosion rate, the most accurate and precise method is probably that of weight loss. This is because the experimentation is easy to replicate and, although long exposure times may be involved, the relatively simple procedure reduces the propensity to introduce systematic (determinate) errors [1,2].

Given sufficient quantitative information about the electrochemical processes occurring, mixed potential theory can be used to predict a corrosion rate. In general, experimental measurements must be made that can be interpreted in terms of mixed potential theory. The most common of these measurements in electrochemical corrosion engineering is the polarization curve. Correlation of electrochemical measurements to as many varied measurements as possible is

good practice. Whereas electrochemical measurements may be the most rapid, they are also the most susceptible to variations in conditions.

The impossibility of a direct measurement of corrosion rate using electrochemical testing would seem to be discouraging. Application of mixed potential theory allows determination of the corrosion rate using a method known as Tafel extrapolation [3]. The extrapolation of anodic and/or cathodic Tafel lines for charge transfer controlled reactions gives the corrosion current density,  $i_{\text{corr}}$ , at the corrosion potential,  $E_{\text{corr}}$ . This method is based on the electrochemical theory of corrosion processes, which was developed by Wagner and Traud [4]. However, under some conditions, no well-defined linear range can be obtained on polarization curves, so some difficulties may arise in evaluation of Tafel slopes [5-7].

Two rules of thumb should be applied when using Tafel extrapolation. For an accurate extrapolation, at least one of the branches of the polarization curve should exhibit Tafel (i.e., linear on semilogarithmic scale) over at least one decade of current density. In addition, the extrapolation should start at least 50 to 100 mV away from  $E_{\text{corr}}$ . These two rules improve the accuracy of manual extrapolations [3].

Recently, many studies have been done to investigate the application of potentiodynamic polarization method [8-12]. Although the use of this method has been more conventional in recent years, it is encountered by many restrictions. How to find these restrictions and to investigate the accuracy of Tafel extrapolation is now an important problem in studies of corrosion rate using electrochemical methods.

In this paper, electrochemical aspects of corrosion are briefly reviewed and the corrosion behaviour of carbon steel in 1,2 and 3N  $\text{H}_2\text{SO}_4$  solutions open to air was investigated by using

weight loss method, electrochemical impedance spectroscopy and potentiodynamic polarization to verify the accuracy of corrosion rate data obtained from Tafel extrapolation.

## 2. Materials and Methods

### 2.1. Material

The material for the working electrode (WE) was 1080 carbon steel (nominal comp. 0.75–0.88% C; 0.60–0.90% Mn; 0.04 max P; 0.05 max S). Analytical reagent grade  $\text{H}_2\text{SO}_4$  and distilled water were used to prepare the exactly 1.000, 2.000 and 3.000N acids (standardised with 1.000M NaOH).

### 2.2. Electrochemical Experiments

A glass cell was used for electrochemical experiment and the laboratory temperature was  $25 \pm 1^\circ\text{C}$ . One cell compartment contained the counter electrode (CE) ( $1\text{cm}^2$  Pt-foil) and the other the WE and a Luggin capillary connected to a saturated calomel reference electrode (RE).

Zohner Instrument model IM6eX collects and evaluates experimental data for both potentiodynamic polarization and EIS measurements. For EIS measurement an AC amplitude of 10 mv was applied and data were collected in the frequency range 100 kHz to 500 mHz using 5 points per decade. All EIS are recorded at the open circuit potential, i.e. at the corrosion potential  $E_{\text{corr}}$ . Potentiodynamic measurements were performed at a potential scanning rate of 10 mv/min. The potential range was from -200 mv to 200 mv vs. OCP. Electrochemical measurements contain potentiodynamic polarization and EIS tests performed using three different WE pre-treatments discussed below:

### **2.2.1. Procedure—Method A**

The working electrode (WE) was in the form of a square cut so that the flat surface was the only surface in the electrode. The exposed area to the test solution was 1 cm<sup>2</sup>.

The specimen was abraded with wet SiC paper (initially 400, 500, 800 and 1200 grades and thereafter with 1200 grade alone). The WE was then degreased by immersion in warm acetone, rinsed with water and immediately inserted whilst wet in the cell. The Luggin capillary was adjusted adjacent to (about 1mm from) the WE.

The impedance spectra (EIS) measurements were carried out after 10 min of exposure of the WE in the solutions. Then potentiodynamic polarization curves for the WE in each solution were recorded immediately after the EIS on the electrode without surface treatment.

### **2.2.2. Procedure—Method B**

The procedure was as for method A, except that the 10 min immersion time changed to 90 min.

### **2.2.3. Procedure—Method C**

The procedure was as for method A, except that the WE on immersion was immediately pre-polarized alternatively at 100 mv vs. OCP for 2 min and then at -300 mv vs. OCP for 10 min. The potential was reached a steady value after 30 min. This potential was selected as  $E_{\text{corr}}$ . After that the impedance spectra (EIS) measurements were carried out on the WE in the solutions. Then potentiodynamic polarization curves for the WE in each solution were recorded immediately after the EIS on the electrode without surface treatment.

### 2.3. Weight Loss Experiment

Standard weight loss tests were also carried out under the procedure according to ASTM G31 [13]. Specimens were cut into 50mm×20mm×3mm coupons for immersion tests and three coupons were used for each acid concentration. Before exposure, the samples were mechanically polished using wet SiC paper (initially 400, 500, 800 and 1200 grades and thereafter with 1200 grade alone) and lubricated using distilled water. The polished samples were cleaned with acetone, washed using distilled water, dried in air and stored over a desiccant. The samples were weighed before exposure by means of an analytical and a digital balance with a precision of 0.0001 g for the original weight ( $W_0$ ) and then hung in test solutions for 12 hr. After immersion at these times the corroded specimens were removed from the solutions, cleaned with distilled water and dried. Finally, the coupons were weighed again in order to obtain the final weight ( $W_1$ ).

## 3. Experimental Results and Discussion

Experimental polarization curves and Nyquist plots obtained from corrosion of the WE in several concentrations of  $H_2SO_4$  solutions open to air with described procedure-methods are shown in Fig.1-3 and Fig.4-6, respectively.

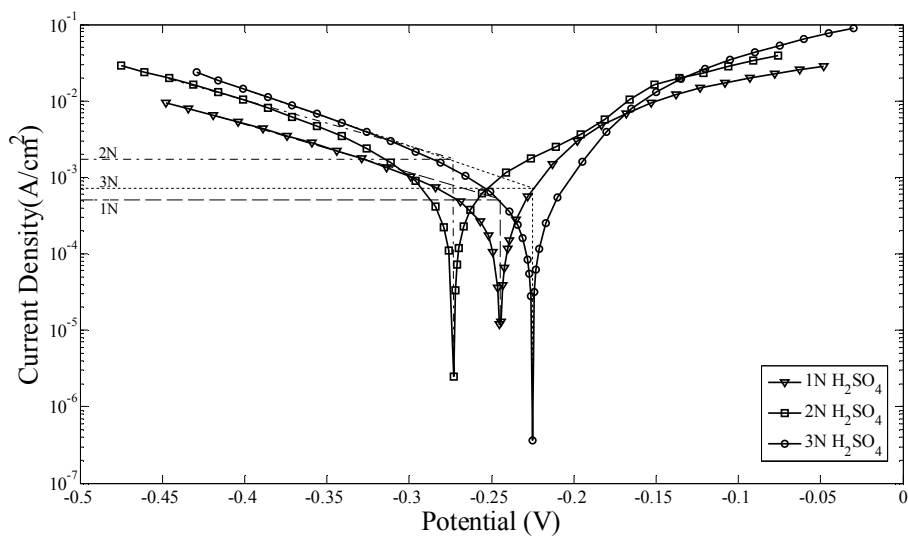


Fig.1. Polarization curves for carbon steel in H<sub>2</sub>SO<sub>4</sub> solutions after 10 min.

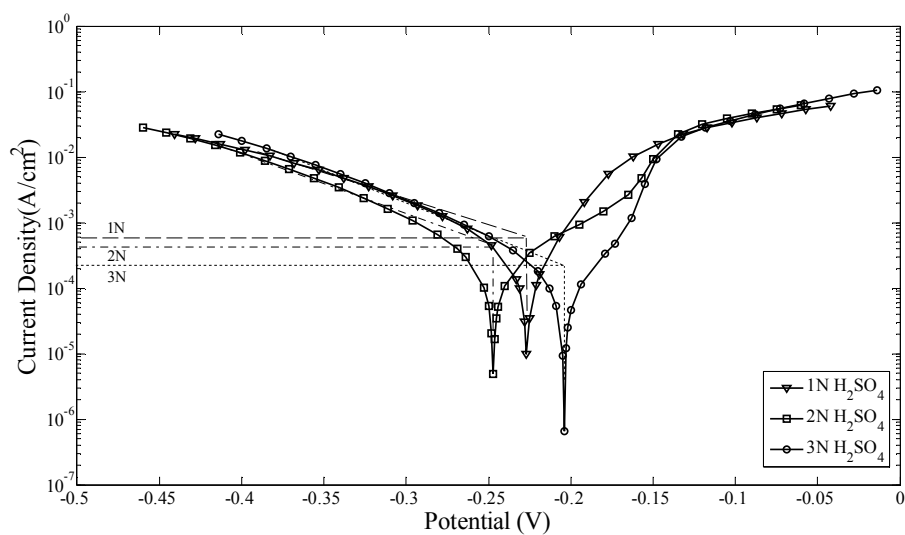


Fig.2. Polarization curves for carbon steel in H<sub>2</sub>SO<sub>4</sub> solutions after 90 min.

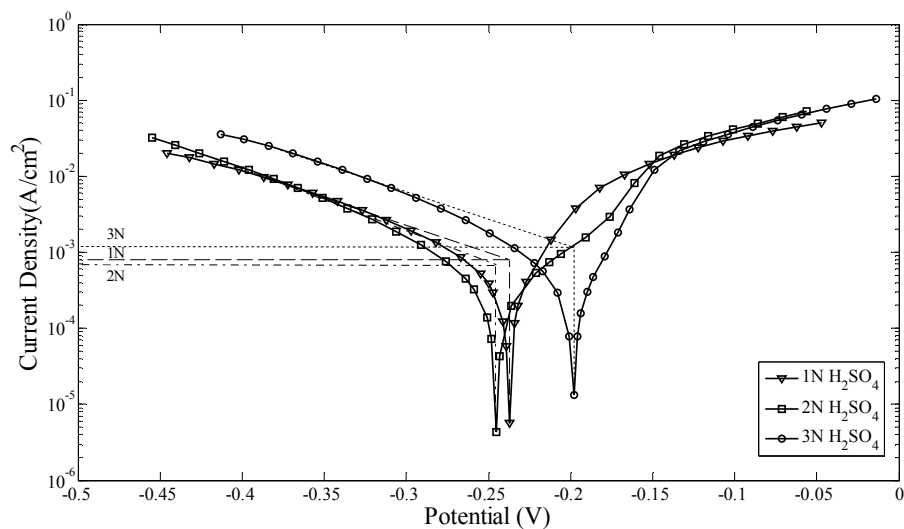


Fig.3. Polarization curves for carbon steel in  $\text{H}_2\text{SO}_4$  solutions after prepolarization.

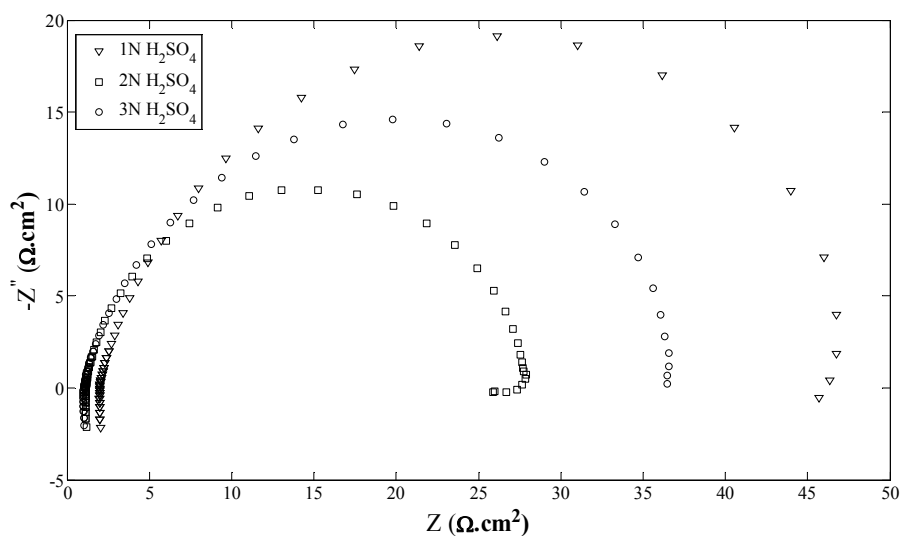


Fig.4. Nyquist plots for carbon steel in  $\text{H}_2\text{SO}_4$  solutions after 10 min.



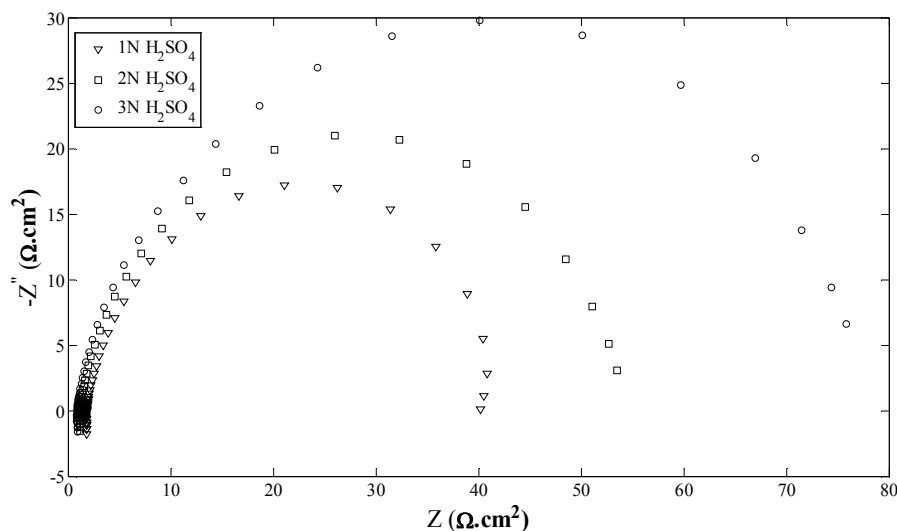


Fig.5. Nyquist plots for carbon steel in  $H_2SO_4$  solutions after 90 min.

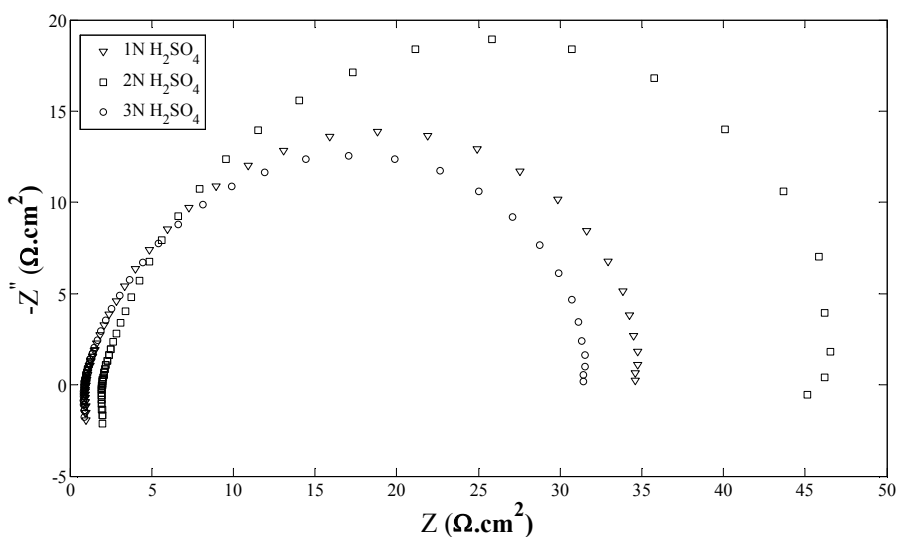


Fig.6. Nyquist plots for carbon steel in  $H_2SO_4$  solutions after prepolarization.

As the conditions at the metal/solution interface approach steady state, the time-rate of change in  $E_{corr}$  decreases. A reasonable criterion for steady state would be a change of less than 5 mV in  $E_{corr}$  over a 10 minute period [3]. According to this criterion all the values of measured  $E_{corr}$  for

procedure-methods A to C have reached to steady state.

It was established from experimental polarization curves that over the experimental potential range (-200 mV to 200mV vs. OCP) the cathodic portions of the curves were indicative of activation polarization and only the following single half cell reactions occur:



As a result of this cathodic activation polarization, the cathodic Tafel lines were extrapolated to corrosion potential to determine corrosion current density ( $i_{corr}$ ).

The values of measured  $E_{corr}$ , calculated  $i_{corr}$  and polarization resistance ( $R_p$ ) for procedure-methods A to C and calculated values of  $i_{corr}$  from weight loss method are shown in Table 1.

It is expected here that corrosion products formed on the metal surface be protective and while  $R_p$  increases over immersion time the corrosion rate decreases; however data obtained from electrochemical measurements do not meet this expectation. As illustrated in Table 1 the  $i_{corr}$  and  $R_p$  of the WE are severely decreased and increased respectively in 2 and 3N  $H_2SO_4$  with the immersion time, while  $i_{corr}$  and  $R_p$  of the WE, show slight increase and decrease respectively from 10 to 90 min immersion time in 1N  $H_2SO_4$ . This shows that the corrosion product formed on the metal surface after 10 min is more protective than that of formed after 90 min in 1N  $H_2SO_4$ .

Table 1: Polarization resistance values obtained by EIS method and corrosion rates determined by the Tafel extrapolation and weight loss methods

Environment	R <sub>p</sub> EIS measurement ( $\Omega \cdot \text{cm}^2$ )			i <sub>corr</sub> Tafel method ( $\mu\text{A}/\text{cm}^2$ )			Av. i <sub>corr</sub> weight loss method ( $\mu\text{A}/\text{cm}^2$ )
	Method A	Method B	Method C	Method A	Method B	Method C	
1 N H <sub>2</sub> SO <sub>4</sub>	51.404	40.562	35.1642	512	621	814	274
2 N H <sub>2</sub> SO <sub>4</sub>	29.894	54.684	46.0848	1612	433	697	346
3 N H <sub>2</sub> SO <sub>4</sub>	41.014	79.8031	31.9306	716	228	1115	457

Regarding method C, the prediction of corrosion behaviour of C.S in H<sub>2</sub>SO<sub>4</sub> is made more severe. Comparing data obtained from this method and methods A and B (as illustrated in Table 2) indicates that no relation exists among the values of data obtained from these three methods in 1, 2 and 3N H<sub>2</sub>SO<sub>4</sub>. Wide distribution ranges of corrosion current densities and polarization resistances demonstrate how electrochemical measurements are susceptible to pre-treatment.

Table 2: Comparison of electrochemical measurements

Environment	Current densities comparison	R <sub>p</sub> values comparison
1 N H <sub>2</sub> SO <sub>4</sub>	C > B > A	A > B > C
2 N H <sub>2</sub> SO <sub>4</sub>	A > C > B	B > C > A
3 N H <sub>2</sub> SO <sub>4</sub>	C > A > B	B > A > C

Since weight loss method is the most accurate method for evaluating uniform corrosion measurements and examination of surface of corroded specimens confirmed that specimens were corroded uniformly in H<sub>2</sub>SO<sub>4</sub> solutions open to air, weight loss method was selected as a criterion for investigating corrosion rates obtained from Tafel extrapolation method. Average corrosion current densities obtained from weight loss tests are also shown in Table 1.

Comparing values of corrosion rates from weight loss and Tafel extrapolation methods indicates that only in the case of 3N H<sub>2</sub>SO<sub>4</sub> - method B the  $i_{\text{corr}}$  obtained from Tafel extrapolation is less than that of weight loss method and this can be explained by the formation of a very protective oxide layer on the metal surface after 90 min immersion time. Except this case, in all other conditions the  $i_{\text{corr}}$  values obtained from Tafel extrapolation are higher than the values of corrosion rates from weight loss method.

#### 4. Conclusion

- Corrosion current densities obtained from Tafel method with three different WE pre-treatment were far from each other and no specified relation were observed among these data.
- Performing EIS measurement just before potentiodynamic polarization tests shows that  $R_p$  values from EIS measurements are in good agreement with  $i_{\text{corr}}$  values from Tafel method; and the more the  $R_p$ , the less the  $i_{\text{corr}}$ .
- The comparison of data obtained from WL and Tafel methods indicates that corrosion rates from Tafel method have usually greater values than those obtained from WL method and this is the only remarkable relation among these two sets of data.
- The susceptibility of electrochemical measurement to pre-treatment as well as other variations in condition implies that corrosion rate estimated based on Tafel extrapolation should be compared to weight loss measurement whenever possible and it is better to use from potentiodynamic polarization for monitoring instantaneous corrosion rate, but not general corrosion rate.

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