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## RESEARCH NOTE

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# EVIDENCE OF THE POTENTIAL SHIFT MECHANISM IN CREVICE CORROSION

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**Abstract** Previous research has indicated a qualitative resemblance between the current distribution along actively corroding crevice walls and currents measured in corresponding anodic polarization plots. Using detailed measurements of the potential gradient along the crevice, a semi-quantitative current distribution was calculated for the crevice wall using a double numerical differentiation method. The calculated current distribution was found to approximate that of the active loop measured in independent anodic polarization tests of the free metal surface.

**Key Words** Crevice, Potential, Corrosion, Current Distribution, Double Numerical Differentiation, Polarization

**چکیده** تحقیقات در گذشته نشان داده است که تشابه کیفی بین توزیع جریان در طول دیواره های خوردگی شیارهای فعال و جریانهای اندازه گیری شده معادل با منحنیهای پلاریزاسیون آندی وجود دارد. در این پژوهش با استفاده از اندازه گیریهای کامل گرادینانت پتانسیل در طول شیار، توزیع جریان نیمه کمی برای دیوار شیار با استفاده از متد دیفرانسیل عددی مضاعف محاسبه شد. در این پژوهش مشخص شد که توزیع جریان محاسبه شده تخمین نزدیکی به جریانی است که برای حلقه فعال اندازه گیری شده از سطح آزاد فلز توسط تستهای مستقل پلاریزاسیون آندی بدست آمده است.

## INTRODUCTION

Large potential shifts within crevices (and pits) have been shown to be responsible for sustained crevice corrosion in the presence of an oxidant or anodic protection. More specifically, if an electrolyte/metal combination contains an active/passive transition in its anodic polarization behavior, sustained crevice corrosion occurs when the potential drop within the crevice,  $IR$ , is greater than a critical potential shift  $\Delta\theta^*$ , rendering the crevice potential,  $E(x)$ , less noble than the passivation potential,  $E_p$  [1]. This mechanism has been proven quantitatively through the use of thin

Luggin probes to measure potential gradients within crevices, while exposed to active crevice corrosion conditions [2,3]. In addition, the anodic current distribution along the crevice wall, inferred from the metal loss profile, was shown to qualitatively compare to the shape of the corresponding anodic polarization curve. In this paper, as a further test of the validity of the potential shift mechanism, a procedure to mathematically calculate the current distribution, from the potential distribution, from the potential distribution within actively corroding crevices, has been applied to an experimental system. The results described here agree with the observed morphology

of the corroded crevice wall and semiquantitatively match the shape of the anodic polarization diagram.

To determine the current distribution along an actively corroding crevice wall, the parameters governing current flow must first be examined. Equation 1 applies to a crevice of uniform width ( $w$ ) and thickness ( $t$ ), filled with a constant conductivity solution, where  $t \ll w$  (one-dimensional approximation).

$$I(x) = \sigma \times t \times w \times dE/dx \quad (1)$$

Where, with an appropriately chosen sign convention:  $I(x)$  = current flowing within the crevice electrolyte toward the opening ( $A$ ),  $dE/dx$  = Electric field,  $d\Phi/dx$ , within the crevice electrolyte ( $V/cm$ ) and  $\sigma$  = Electrolyte conductivity ( $ohm^{-1}cm^{-1}$ ).

These conditions were approximated in previous experiments [1-3] and in the present work for crevices whose depth,  $x_0$ , is greater than some critical distance,  $x_c$ , for the crevice corrosion criterion,  $IR > \Delta\Phi^*$ , to be met, as shown elsewhere [4]. Accordingly, if  $\sigma$  is constant, the change in  $I(x)$  as a function of distance into the crevice may be represented as:

$$dI(x) = \sigma \times t \times w \times \left( \frac{dE}{dx} \Big|_{x+dx} - \frac{dE}{dx} \Big|_x \right) \quad (2)$$

The change in the current in the depth direction must be matched by the current originating or terminating in the section at depth  $dx$  of the crevice wall for a one-sided metal crevice (as encountered, for example, in organic coated metal and experimental arrangement used here):

$$dI(x) = i_0(x) \times w \times dx \quad (3)$$

and therefore,

$$i_0(x) = \sigma \times t \times \frac{d^2E}{dx^2} \quad (4)$$

where  $i_0(x)$  = current density on the crevice wall ( $A/cm^2$ , with the sign convention used,  $i_0$  is positive for anodic currents).

## EXPERIMENT

This approach was examined using an established crevice geometry [1-3] and a carbon steel of a type relevant to the ongoing investigation [5]. A specimen of reinforcing rebar, meeting ASTM A615-86 specifications for chemical composition (see Table 1), was placed into a chemically inert artificial crevicing apparatus (see Figure 1) with predetermined crevice dimensions of 10 mm (depth)  $\times$  5mm (width)

TABLE 1. Chemical Composition of the Reinforcing Rebar Steel Specimen (Wt%).

C	0.33	Si	0.19
Mn	0.97	Cr	0.11
P	0.01	Cu	0.027
S	0.02	Ni	0.1
V	0.003	Sn	0.001

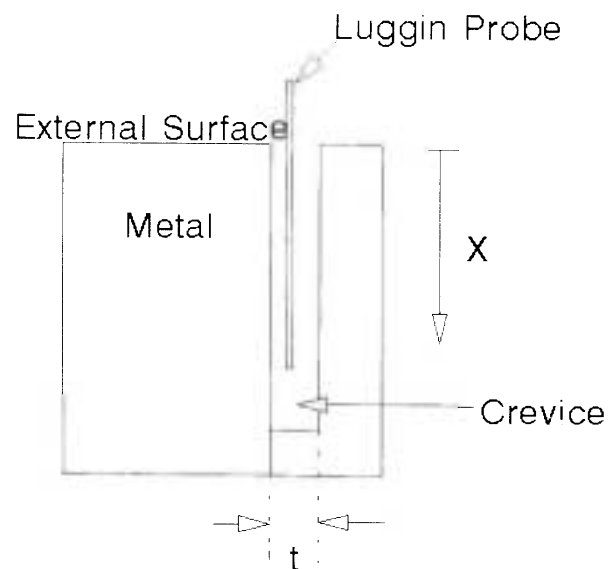


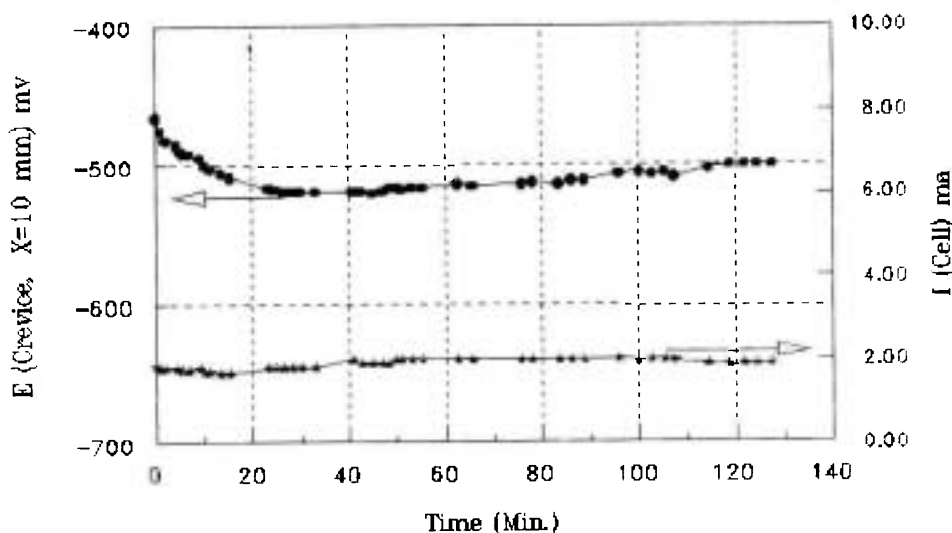
Figure 1. A schematic diagram of crevice design.

×0.5 mm (thickness). The crevice apparatus consisted of a teflon mount with a plexiglas crevice wall, enabling visual observation of the crevice corrosion occurring on the opposite wall (steel) of the crevice. One other surface, the steel sample was exposed to the aqueous environment external, to the crevice. A protective lacquer was used to ensure that the solution contact was not made with the remaining four sides of the rectangularly shaped steel sample, which were enclosed within the Teflon mount. Appropriate electrical connections were made to enable polarization of the sample. The apparatus was submerged in a pH 4.7 acetic acid buffer solution (0.5M CH<sub>3</sub>COOH + 0.5M CH<sub>3</sub>COONa), prepared from reagent grade chemicals and distilled water. The solution had a conductivity of  $30.5 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$ . While the external, exposed surface of the sample was anodically polarized in the passive regime of the anodic polarization diagram, a Luggin probe, with a tip diameter of approximately 0.05 mm, was used to record the potential at 0.25 mm intervals within the crevice. A crevice potential profile was then experimentally obtained.

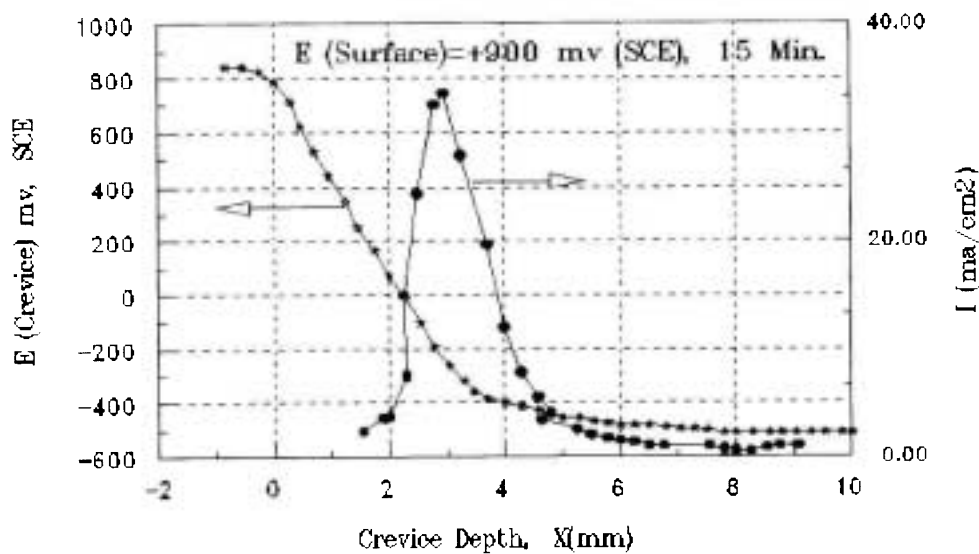
## RESULTS

The results presented here are typical of multiple experiments conducted. Visual observation indicated that the external steel surface, while polarized at +900 mv vs saturated calomel electrode (SCE), was in the passive state while portions of the sample within the crevice actively corroded. Figure 2 illustrates the potential at the crevice bottom (x=10mm, see also Figure 3 insert) and the total cell current as a function of time. Clearly, a potential drop exceeding 1 volt is present within the crevice for duration of the experiment. In addition, the cell current of approximately 2 mA corresponds to currents present under active corrosion conditions, but from visual observation and other research [1-3], the current distribution within the crevice is not uniform. An actively corroding zone developed starting typically 2-4 mm from the crevice opening.

The potential gradient within the crevice was measured and is demonstrated in Figure 3. This gradient is primarily linear between the crevice opening and the active/passive transition within the



**Figure 2.** Potential at the crevice bottom and total current as a function of time with the exterior surface polarized at +900 mv (SCE).



**Figure 3.** Measured crevice potential and calculated crevice current (X) profiles with the exterior surface polarized at +900 mv (SCE). The active/passive corrosion transition lies approximately at 2.5 mm.

crevice. Deviations from linearity exist near the crevice opening (due to the end effects) and the active corrosion region of the crevice. From the slope of the linear region, the total cell current was estimated by using Equation 1. The result fell within approximately 35% of the values reported in Figure 2. The effectiveness of this estimate is limited by the precision of the machined crevice dimensions in the plexiglas, positioning of the crevice with respect to the metal sample and the amount of the passive current originating from the free metal surface.

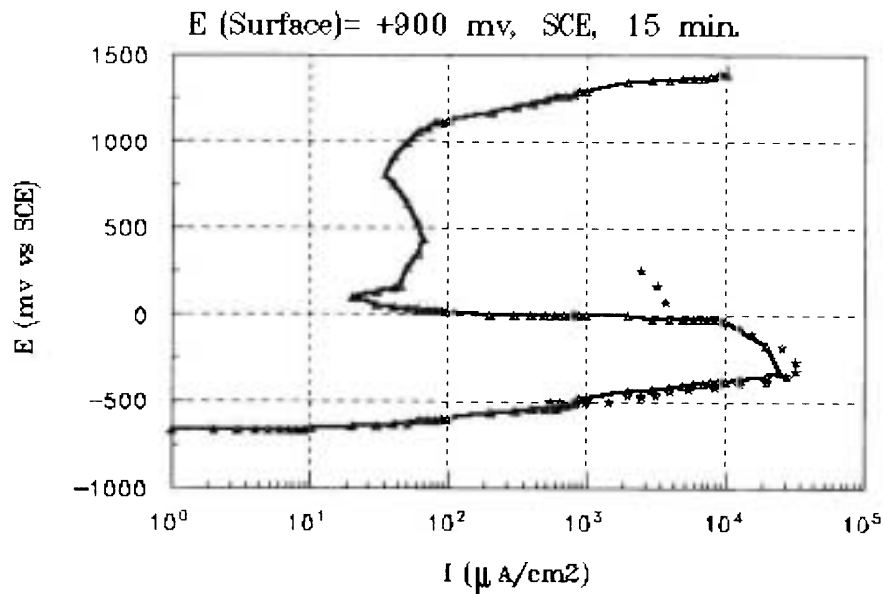
Equation 4 was applied to the potential data in Figure 3. The second derivative of potential with respect to depth was evaluated numerically using a sequence of 5-point computation algorithms [6]. The first 5-point derivative computation (Equation 5) was performed on the potential with respect to depth to obtain the electric field ( $\text{vcm}^{-1}$ ) distribution within the crevice.

$$\frac{dE}{dx} \Big|_{x=i\Delta x} = \frac{2 \times (E_{i+2} - E_{i-2}) + (E_{i+1} - E_{i-1})}{10 \times \Delta x} \quad (5)$$

Where  $E_i$  designates the potential at a point  $i\Delta x$  away from the crevice opening, with  $\Delta x = 0.025\text{cm}$ . The second 5-point derivative computation was completed using the results from Equation 5 as shown in Equation 6.

$$\frac{d^2E}{dx^2} \Big|_{x=i\Delta x} = \frac{2 \times \left( \frac{dE}{dx} \Big|_{i+2} - \frac{dE}{dx} \Big|_{i-2} \right) + \left( \frac{dE}{dx} \Big|_{i+1} - \frac{dE}{dx} \Big|_{i-1} \right)}{10 \times \Delta x} \quad (6)$$

The result of Equations 5 and 6 is an effective 9-point data smoothing algorithm which can be used to calculate the current distribution within the crevice. Only potential data from points on crevice-width (0.5mm), or further, from the crevice opening were used in Equation 5 to avoid end effect errors. In addition, because a 9-point method was used, the first calculated  $i_0(x)$  value corresponds to a point which is 1.5 mm away from the crevice opening. The computed current distribution on the crevice wall is shown in Figures 3 and 4. Figure 3 illustrates the relationship between the crevice potential and computed crevice currents superimposed on an anodic polarization



**Figure 4.** Calculated crevice current distribution (X) superimposed on the anodic polarization curve for the reinforcing bar steel/pH 4.7 acetic acid buffer system measured under deaerated conditions at a scan rate of 0.1 mv/sec.

curve, measured at 0.1 mv/sec. scan rate, of a rebar steel specimen, of the same composition while was used in the crevice experiment, in deaerated pH 4.7 acetic acid solution. A good agreement is found between the magnitudes of the calculated currents and those measured during anodic polarization. This type of calculated current distribution also strongly agrees with the qualitative current distribution observed under in-situ and ex-situ observation [3].

The accuracy of the computed current distribution is limited by the experimental scatter in the potential-position data, knowledge of exact crevice dimensions, solution conductivity and the type of derivative computation algorithm used. Deviation from the assumptions used in the calculations may result in more serious errors. For example, the accumulation of ions and corrosion products within the crevice may alter the solution conductivity as a function of distance into the crevice and the size and shape of the active loop of the anodic polarization curve. In that case, Equation 2 is only an approximation. Likewise,

deviations from an ideal one-dimensional crevice geometry are expected to introduce additional error. A more refined treatment of the problem should include allowance for these factors.

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