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# 85

GROWTH RATE OF CALCAREOUS DEPOSITS UPON CATHODICALLY  
POLARIZED STEEL IN SEAWATER

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ABSTRACT

Experiments have been performed where a series of flat, 1018 steel specimens were cathodically polarized in seawater to either  $-0.85\text{v.}$  or  $-1.00\text{v.}$  (SCE). Individual tests were terminated after from 1.5 to 1560 hours, and the calcareous deposit thickness was measured by edge viewing of the specimen in a scanning electron microscope. The film thickening behavior has been characterized for each of the two potentials and correspondences between current density changes during the experiment and ultimate deposit thickness are discussed. Where appropriate, the results are related to marine cathodic protection technology.

INTRODUCTION

The importance of calcareous deposits to the effective and efficient operation of seawater cathodic protection systems is generally recognized (1). Thus, these surface

films form upon cathodic surfaces as a consequence of the relatively high pH which may exist here ( $\text{pH} \approx 10-12$ ) and the fact that the solubility limit for most inorganic compounds, such as  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ , decreases with increasing pH (2). Calcareous deposits are of particular benefit because of reduced net cathodic protection current and enhanced throwing power or more uniform spreading of current (3). Any variable which influences rate of the cathodic reaction(s), pH at the metal-seawater interface, the pH profile into the electrolyte and composition and properties of the electrolyte may influence these deposits. Such factors include temperature (4,5), magnitude of polarizing potential or current (6,7), flow state (6,8), seawater chemistry (9,10) and substrate chemistry (2,7). A recent comprehensive literature review of calcareous deposits (11) has been presented, and it was concluded that our understanding of these surface films, in perspective to their engineering importance, is shallow. The purpose of the research presented here has been to characterize the thickening

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properties for calcareous deposits under select conditions and to rationalize the importance of deposit thickness with regard to cathodic protection effectiveness and efficiency.

#### EXPERIMENTAL PROCEDURE

Specimens were prepared from commercial, 6.3 mm thick 1018 steel by sectioning and machining. A set of preliminary specimens measuring 7.6 x 24.6 mm were prepared and tested; however, scatter in the current density data prompted increasing the size to 21.5 x 49.0 mm. The latter specimens proved more satisfactory, and so all subsequent experiments employed these. The specimen surface to be exposed was ground and polished with #600 SiC paper. A lead wire was then soldered to the top specimen edge and all edges and faces other than the polished one were given a vinyl coating (Quelspray). Prior to application of the coating and again before immersion specimens were cleaned with alcohol.

Three different size plastic baths with lengths of 30, 37, and 38 cm, widths of 26, 16 and 7 cm, respectively, and a water depth of 5 cm were employed for the exposures. Water entered at one end, passed through a baffle to spread the flow and proceeded along the length direction to an overflow at the other end. The flow rate was approximately 1 l/min in all cases. The electrolyte was sand-filtered, once-through natural seawater, as is available at the Center for Marine Materials Laboratory. Properties of this water for an annual cycle have been reported previously (12). No attempt was made to control temperature during the experiments, and this ranged from 21 - 25°C.

Potential was controlled during the experiments at either -0.85v. or -1.00v. versus a commercial saturated calomel electrode. This was accomplished by employing locally fabricated potentiostats based upon the circuit diagram of Baboian (13) in conjunction with a platinum coated niobium counter electrode. Potential was routinely monitored with an Orion 701A Digital Multimeter, and applied current was recorded by an Esterline

Angus PD 2064 Data Acquisition System. Upon termination of a particular experiment the specimen was removed from the bath, rinsed with alcohol and placed in a desiccator.

A total of eleven large and fifteen small specimens were polarized at -1.00v. and eleven large specimens at -0.85v. Test duration for individual specimens ranged from 1.5 to 1560 hours. Calcareous deposit thickness was characterized by examination in an ISI Super IIIA Scanning Electron Microscope. Specimen preparation involved removal of the vinyl coating and viewing edge-on. Thickness measurements were made at 0.05 mm intervals, either on the phosphor screen or upon micrographs; and the average value was calculated. In excess of forty measurements were recorded for each specimen. In some cases the specimens were surface ground on a plane normal to that of the deposit so that thickness could be measured at locations away from the edge. No systematic variation in deposit thickness with position on the specimen was apparent, however.

#### RESULTS AND DISCUSSION

Current Density Variations. Table I lists general parameters for individual specimens and tests. Figures 1 and 2 present current density data for those specimens polarized to -1.00 and -0.85v., respectively, where the exposure time was in excess of 900 hours. In the former case (-1.00v.) the data are characterized by a relatively high initial current density, which increased with time during the approximate period of 0.1 to 5 hours. Subsequently, current density decreased and achieved an apparent or near-steady state value after about 100 hours. The trends evidenced here are in general agreement with what has been reported in previous work (6, 10). Data for other specimens of this same test group (Table I) were not included in Figure 1 for the purpose of clarity; however, these conformed to and were distributed throughout the scatter ranges exhibited by Specimens 41, 62 and 65. The greatest variations were in the pre-ten hour period, and there was no correlation of the ordering of

current densities for this time range and the long-term, apparent steady-state values. Data for the preliminary experiments involving smaller specimens have not been presented. These conformed to the same trend as in Figures 1 and 2 but with more scatter. This was attributed, at least in part, to the fact that the current density was on the same order as the resolution capability of the instrumentation.

For specimens polarized to  $-0.85\text{v}$ . (Figure 2) the pre-ten hour period was characterized by an approximately constant or slightly decreasing current density with time with a magnitude approximately one-half of the corresponding  $-1.00\text{v}$ . data. Specimens of this test group that have not been included in Figure 2 exhibited current densities during this same time period that were in the range  $150\text{--}700\text{ mA/m}^2$ . The same decrease in current density during the 10-100 hour period to a near steady-state value that was noted at  $-1.00\text{v}$ . occurred at the more positive potential also.

The relatively constant current density during the 0.1-5 hour exposure period at  $-0.85\text{v}$ . and the current density increase during the same time for  $-1.00\text{v}$ . specimens reflect occurrence of a phenomenon which counters the effect of calcareous deposit accumulation and oxygen concentration polarization. A possible factor here is cathodic "cleaning" of the steel surface which may increase the exchange current density for the hydrogen reaction. Such a process is expected to be more significant at the more negative potential; first, because of greater current density and, second, because of an enhanced rate of hydrogen evolution.

While the terms "apparent" or "near-steady state" have been employed with reference to the post-100 hour current density data, it must be emphasized that this parameter was subject to both sudden (note Specimen 18 at 340 hours and Specimen 65 at 280 hours) and gradual (see Specimen 9 for 500-1000 hours) changes. Such behavior is thought to be due to cracking or separation (or both) of the calcareous

deposit. For the specimens tested beyond 500 hours exposure at  $-1.00\text{v}$ . current density ranged from 80 to  $140\text{ mA/m}^2$  with a mean value of  $110\text{ mA/m}^2$ . At  $-0.85\text{v}$ . the range was  $60\text{--}250\text{ mA/m}^2$  with a mean of  $170\text{ mA/m}^2$ . Analysis of the mean and variance for these two sets of data indicated that the above difference is statistically significant, and so it was concluded that a more impermeable deposit was formed at  $-1.00\text{v}$ . than at  $-0.85\text{v}$ . The observation that the near-steady state current density was less at the more negative potential is consistent with the data of Wolfson et al (6), who reported similar ordering in the case of specimens polarized to  $-1.03\text{v}$ . and  $-0.93\text{v}$ . The fact that the above values were 2-3 times greater than typical design current densities for offshore structures in warm, quiescent waters (14), suggests that further decrease of current density would occur if the experiments were extended to longer times.

Figure 3 presents a photograph of typical specimens from the two sets of experiments. The white areas on three of the  $-1.00\text{v}$ . specimens were indicative of separation of the calcareous deposit from the metal surface. Note the extreme state of deposit blistering or rupturing for one of the 96 hour exposure specimens. No coating separation was observed on any of the  $-0.85\text{v}$ . specimens.

#### Calcareous Deposit Thickness.

Figures 4 and 5 present plots of film thickness versus exposure time for the  $-1.00$  and  $-0.85\text{v}$ . experiments, respectively. In the former case data for both the preliminary, small specimens and subsequent large specimens have been included. The data scatter here is relative large, particularly in the long time regime. This may be a consequence of an inherent variability of the phenomenon under investigation. The possibility of an undetected, momentary potentiostat malfunction causing this cannot be ruled out, however. The fact that seawater temperature was not controlled could also have been a factor. The best fit curve in Figure 4 was configured without consideration of the two specimens with greatest deposit

thickness. In doing this the data was interpreted as exhibiting a plateau or constant deposit thickness from approximately 100 hours to the time limit of the experiments (1560) hours. This is consistent with the current density-time plots (Figure 1), where a near-steady state value was observed subsequent to this same exposure duration.

The limited amount of thickness data at  $-0.85\text{v.}$ , combined with the scatter, makes it difficult to confirm that the same deposit thickness-time character was exhibited, although the curve that was drawn through this data assumed this to be the case. On this basis the deposit thickening rate during the growth period was greater for specimens polarized to  $-1.00\text{v.}$  compared to  $-0.85\text{v.}$ , as should be expected since current density was greater in the former case during this time interval. Thus, it may be reasoned that initial deposit thickening rate increased in proportion to current density. For the range of exposure times investigated the mean calcareous deposit thickness at  $-1.00\text{v.}$  exceeded that at  $-0.85\text{v.}$  by an approximately constant amount of  $0.3 \times 10^{-5}\text{m.}$  In the post-one hundred hour regime this amounts to only a fifteen percent difference. This thickness distinction presumably resulted from the higher current density during the initial exposure period for specimens polarized to  $-1.00\text{v.}$  compared to those at  $-0.85\text{v.}$  No correlation could be made, however, between the current density and deposit thickness for individual specimens, either in the post-or pre-100 hour regimes.

In cases where more than one deposit layer was observed the film thickness measurements were the sum of the thickness of individual layers. Thus, the data in Figure 4 do not include the thickness of the intermediate electrolyte between successive regions of deposit. This probably accounts for the difference between the present film thickening behavior (Figures 4 and 5) and that observed by Wolfson et al (6), where deposit thickness increased with time for at least the first 400 hours of

exposure. In the latter experiments film thickness was measured by a stylus technique, and so the measured values included any electrolyte layer(s) beneath a disbonded film.

The fact that mean thickness of the calcareous deposit layer(s) for the post-100 hour period at  $-1.00\text{v.}$  was fifteen percent greater than at  $-0.85\text{v.}$  presumably resulted from the higher current density at the former potential during the earlier (pre-100 hour) time. The observation that current density was thirty-five percent greater at the more positive potential compared to  $-1.00\text{v.}$  subsequent to 500 hours could be due to a higher resistivity for the deposit formed at the more negative potential. An alternative explanation however, is that where deposit separation occurred in the case of  $-1.00\text{v.}$  specimens the electrolyte between different calcareous deposit layers was void of significant convective mixing with the bulk solution and oxygen concentration polarization was accordingly enhanced. On this basis it may be that the confined electrolyte and not the calcareous deposit per se was responsible for the reduced current density at  $-1.00\text{v.}$

The edge-on scanning electron microscopy viewing of specimens revealed a range of calcareous deposit morphologies which were not clearly correlatable with exposure time. In some cases deposit thickness was irregular, as shown by Figure 6, while in others it was relatively uniform (Figure 7). Of particular interest morphologically were areas where deposit separation had occurred. One such region is illustrated in Figure 8. Typically, the thickness of the separated layer was uniform and in the range  $1.0-1.4 \times 10^{-5}\text{m.}$  Also, these layers appeared more dense than films that were still contiguous with the steel surface. Figure 8 reveals that the second generation layer nucleated and grew from or very close to the metal surface. Deposit disbonding was only observed for specimens polarized to  $-1.00\text{v.}$ , with all deposits formed at  $-0.85\text{v.}$  appearing integral with the metal surface.

Two possible explanations have been considered for the observed disbonding of deposits. The first considers that growth impingement from adjacent areas caused internal stress with a component normal to the metal surface of sufficient magnitude that the bond strength of the metal-deposit interface was exceeded. However, the observation that the mean near-steady state current density and long-term deposit thickness were not greatly different for specimens polarized at each of the two potentials investigated tends to discount this. Alternatively, it may be reasoned that gas evolution at the deposit-metal interface as a consequence of the cathodic hydrogen reaction was responsible. Such a mechanism is analogous to that projected to cause delamination of coatings on metals as a consequence of excessive cathodic protection. The fact that disbonding was observed only for specimens polarized to  $-1.00\text{v.}$  and not  $-0.85\text{v.}$  is consistent with this. The possibility cannot be ruled out, however, that disbonding may occur also at the latter potential for exposure times in excess of the ones considered here.

It may be reasoned that the variations in current density with time for individual specimens in Figures 1 and 2, particularly in the near-steady state regime, (see, for example, the data for Specimen 1 at approximately 250 hours exposure), were probably associated with cracking of deposits, as shown, for example, by Figure 9. Such a process is analogous to that which has been projected to occur in the case of localized breakdown and repair of a passive film (15). That these fluctuations were of approximately the same magnitude for each of the two potentials indicates that disbonding per se was not a contributing factor. A disbonded coating such as in Figure 8 probably continued to serve as an effective diffusion barrier for critical species such as  $\text{O}_2$  and  $\text{OH}^-$ . In addition, the confined electrolyte layer beneath a separated deposit may also be important, as discussed above. For exposures involving greater electrolyte movement, however, such separated

deposits may become removed and therefore should be less effective in affording protection. This follows since the adherence of a disbonded deposit segment to the metal and to adjacent deposits may be exceeded by a sufficiently severe flow state. On this basis, changes in cathodic current demand with increasing velocity should be greater at more negative potentials where disbonding occurs than at more positive values where it apparently does not.

#### CONCLUSIONS

1. For steel specimens cathodically polarized under the experimental conditions investigated current density remained relatively constant or increased during the initial five hours of exposure. Variations of this parameter from one specimen to the next were particularly apparent during this same period. Current density decreased between 10 and 100 hours but was relatively constant from 100 to 1560 hours, the latter being the maximum exposure time for the experiments. Current fluctuations during this latter period are thought to be due to occurrence and repair of cracks in the deposit.
2. The thickness of calcareous deposits increased during the initial 100 hours of exposure, the rate being more rapid of  $-1.00\text{v.}$  than at  $-0.85\text{v.}$  Between 100 and 1560 hours deposit thickness was constant.
3. Disbonding of calcareous deposits and subsequent growth of a new deposit layer at the steel surface occurred for specimens polarized to  $-1.00\text{v.}$  but not  $-0.85\text{v.}$  The diffusion zone associated with the electrolyte beneath such deposits was probably responsible for the observation that at long times less current density was required to polarize specimens to  $-1.00\text{v.}$  than  $-0.85\text{v.}$  Removal of disbonded deposits under conditions of adequately severe relative motion between the metal and electrolyte and consequent mixing of solution beneath such layers with the bulk may be an important consideration in determining current demand in flow situations.

#### ACKNOWLEDGEMENT

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Table I

| Specimen Number | Specimen Size* | Potential, v. (SCE) | Exposure Duration, hrs. |
|-----------------|----------------|---------------------|-------------------------|
| 1               | Small          | -1.00               | 3                       |
| 2               | "              | "                   | 6                       |
| 3               | "              | "                   | 12                      |
| 4               | "              | "                   | 18                      |
| 5               | "              | "                   | 20                      |
| 6               | "              | "                   | 24                      |
| 7               | "              | "                   | 48                      |
| 8               | "              | "                   | 72                      |
| 9               | "              | "                   | 120                     |
| 10              | "              | "                   | 192                     |
| 11              | "              | "                   | 624                     |
| 12              | "              | "                   | 720                     |
| 13              | "              | "                   | 936                     |
| 11L             | Large          | -0.85               | 6                       |
| 2L              | "              | "                   | 13                      |
| 3L              | "              | "                   | 36                      |
| 4L              | "              | "                   | 120                     |
| 5L              | "              | "                   | 360                     |
| 6L              | "              | "                   | 888                     |
| 7L              | "              | "                   | 960                     |
| 8L              | "              | "                   | 1032                    |
| 9L              | "              | "                   | 1032                    |
| 10L             | "              | "                   | 1032                    |
| 11L             | "              | -1.00               | 6                       |
| 12L             | "              | "                   | 48                      |
| 13L             | "              | "                   | 96                      |
| 14L             | "              | "                   | 96                      |
| 15L             | "              | "                   | 96                      |
| 16L             | "              | "                   | 240                     |
| 17L             | "              | "                   | 888                     |
| 18L             | "              | "                   | 1128                    |
| 19L             | "              | "                   | 1488                    |
| 20L             | "              | "                   | 1560                    |

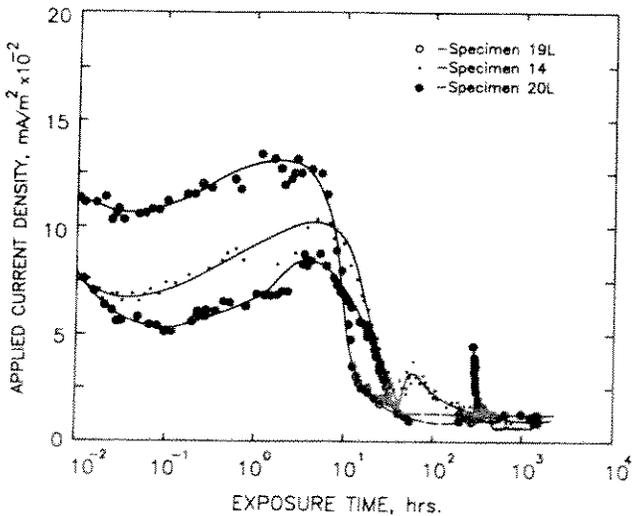


Figure 1: Applied current density versus exposure time for specimens polarized to -1.00v. (SCE), where time exceeded 900 hours.

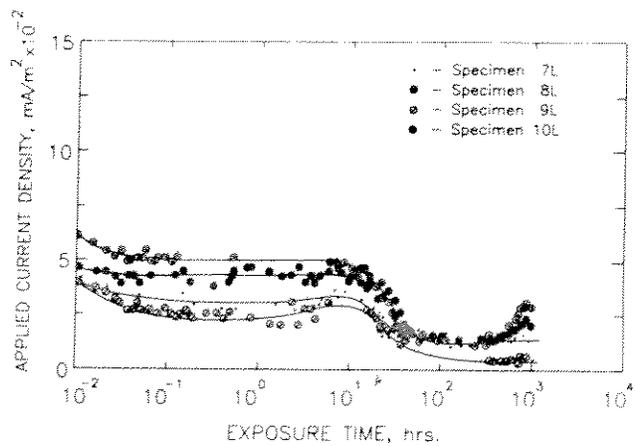
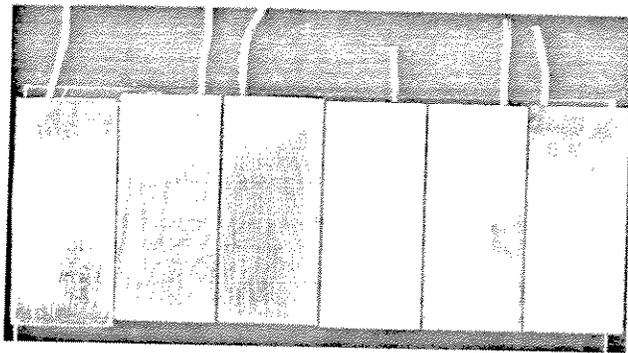
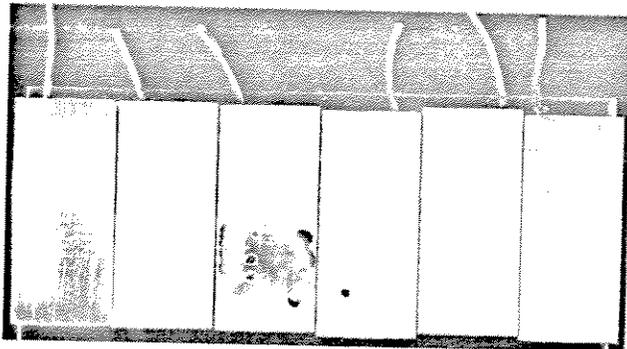


Figure 2: Applied current density versus exposure time for specimens polarized to -0.85v. (SCE), where time exceeded 900 hours.



AS POLISHED 6h 13h 36h 120h 360h

(a)



AS POLISHED 96h 96h 96h 48h 6h

(b)

Figure 3: Photographs of specimens subsequent to exposure: (a)  $-0.85\text{v.}$  specimens and (b)  $-1.00\text{v.}$  specimens

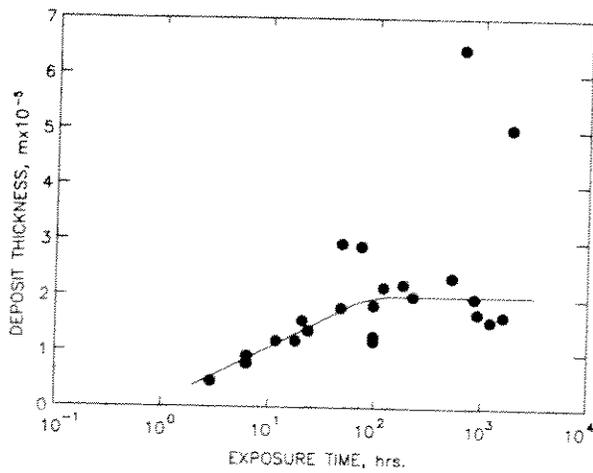


Figure 4: Calcareous deposit thickness versus exposure time for specimens polarized to  $-1.00\text{v.}$  (SCE).

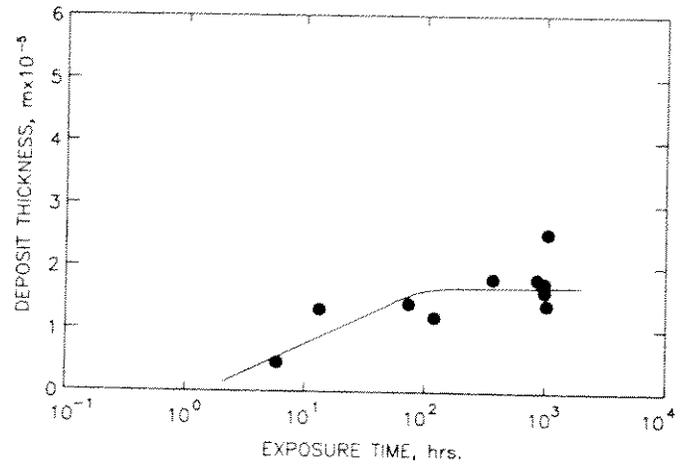


Figure 5: Calcareous deposit thickness versus exposure time for specimens polarized to  $-0.85\text{v.}$  (SCE).

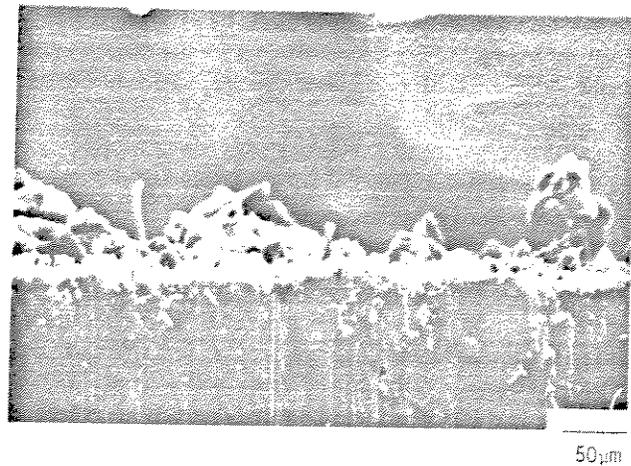
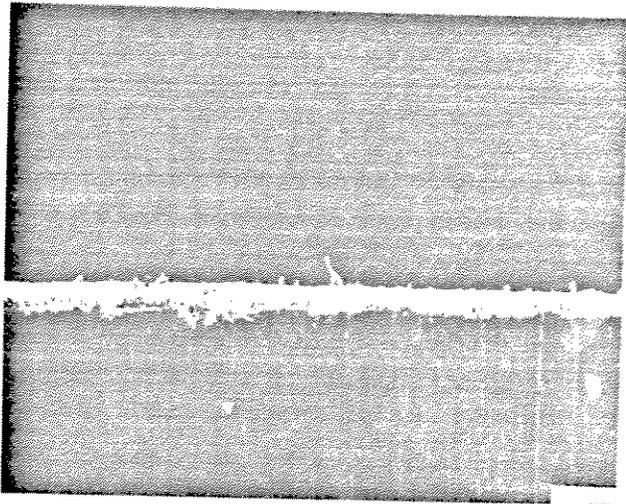


Figure 6: Edge SEM view of Specimen 1 (3 hour exposure at  $-1.00\text{v.}$  (SCE)) and calcareous deposit showing irregular thickness profile.



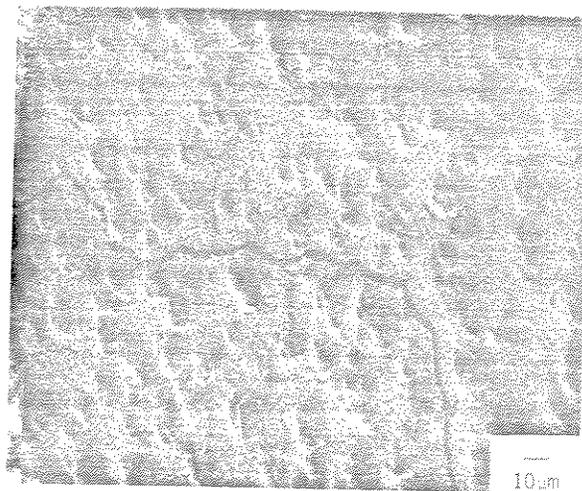
10 $\mu$ m

Figure 7: Edge SEM view of Specimen 6 (24 hour exposure at -1.00v. (SCE)) showing uniform thickness profile.



10 $\mu$ m

Figure 8: Edge SEM view of Specimen 20L (1560 hours exposure at -1.00v. (SCE)). Note disbonded calcareous deposit layer and second generation deposit emanating from metal surface .



10 $\mu$ m

Figure 9: Edge SEM view of crack in calcareous deposit. Micrograph courtesy of M. Kunjapur.