FINAL REPORT

REPAIR OF CRACKS IN CONCRETE BY ELECTROCHEMICAL ACCRETION OF MINERALS FROM SEAWATER: A FEASIBILITY STUDY

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16. Abstract
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The results established that the electrochemical accretion processes can be utilized to seal undesirable cracks in concrete piles located in marine environments. Unfortunately, even the lowest accretion current (1.0 uA/sq mm) used in the study appeared to be too high, since it induced too rapid a deposition and at wrong locations inside a crack, which led to incomplete sealing. The results implied that a significantly lower accretion current, which is probably close to that typically used in a cathodic protection system for concrete structures, may be all that is needed to achieve complete sealing of any crack in a concrete pile.

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The results established that the electrochemical accretion processes can be utilized to seal undesirable cracks in concrete piles located in marine environments. Unfortunately, even the lowest accretion current (1.0 uA/sq mm) used in the study appeared to be too high, since it induced too rapid a deposition and at wrong locations inside a crack, which led to incomplete sealing. The results implied that a significantly lower accretion current, which is probably close to that typically used in a cathodic protection system for concrete structures, may be all that is needed to achieve complete sealing of any crack in a concrete pile.

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INTRODUCTION

At present, the only procedure that has shown some promise in the repair of cracks in concrete piers and piles located inland is the pressure injection of low viscosity epoxy into the cracks. The effectiveness of this procedure for repairing cracks in concrete piles located in coastal tidal water, where a considerable portion of each pile is constantly submerged in seawater, is questionable. This lack of a proven procedure for repairing cracks in such concrete piles, especially when the cracks are still in the early stage of development, has forced engineers to wait until these have progressed far enough to result in spalling of the concrete. At that time, jacketing of the piles, which is an expensive procedure, is used as a repair procedure of the last resort. This situation points to the need for some new repair procedures, preferably some that can be applied when the cracks are still in the early stage of development. Fortunately, the seawater surrounding the piles offers an unique environment that lends itself to the development of such a procedure, which would rely on the electrochemical accretion of minerals from ions commonly found in seawater in the cracks.

BACKGROUND

Such a procedure would utilize some of the electrochemical reactions that occur when a relatively small amount of direct current (DC) is passed between a pair of electrodes. On most cathodic surfaces in aerated water, the following reduction reaction occurs

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-.$$

However, if the potential between the electrodes is more negative than the reversible hydrogen electrode, the following reaction also occurs

$$\frac{1}{2}O_2 + 2H_2O + 2e^- \rightarrow 2OH^-.$$

In either case, hydroxyl ions are produced on the surface of the cathode. Some of these hydroxyl ions are removed by convection and/or diffusion from the surface of the cathode, thereby causing a decrease in the concentration of these ions with increased distance from the cathode. This concentration gradient around the cathode is influenced by the electrolyte composition, temperature, and flow velocity of the water.

In seawater, the following series of reactions also occur:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$

$$HCO_3^- \rightarrow H^+ + CO_3^{-2}.$$

When hydroxyl ions are added to this system as a consequence of one of the above cathodic processes at the cathode, then the following reactions can occur:

$$H^+ + OH^- \rightarrow H_2O$$

$$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{-2}.$$

In addition, because calcium and magnesium ions are relatively abundant in seawater, the following reactions also occur at the surface of the cathode:

$$CO_3^{-2} + Ca^{+2} \rightarrow CaCO_3\downarrow$$

$$CO_3^{-2} + Mg^{+2} \rightarrow MgCO_3\downarrow$$

$$Mg^{+2} + 2OH^- \rightarrow Mg(OH)_2\downarrow.$$

These reactions lead to the formation of mineral deposits on the cathodic surfaces (see Figure 1). Possibly because of the relatively higher solubility of magnesium carbonate, the mineral deposits consist mainly of 17 to 32 percent aragonite (calcium carbonate) and 40 to 80 percent brucite (magnesium hydroxide), with very small amounts of calcite and halite.[1]

Utilizing these electrochemical reactions, Hilbertz accreted these minerals on cathode substrates such as wire mesh to yield a strong material with an average compressive strength on the order of 29.4 MPa.[2] For the accretion process to occur, the application of only a relatively small amount of electricity

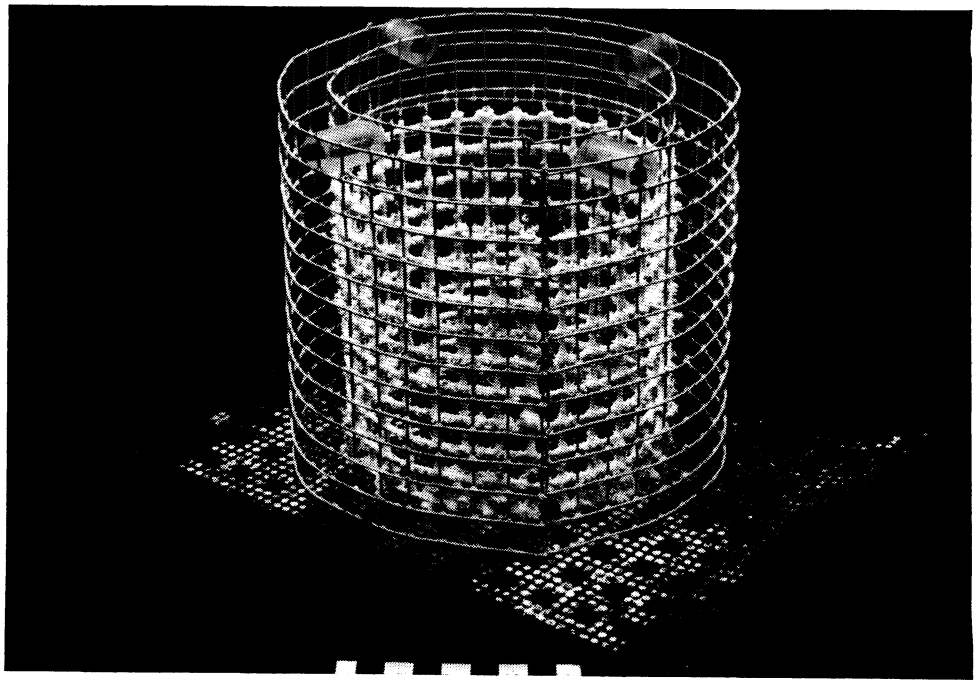


Figure 1. Building of artificial reef by accretion of minerals from seawater on a cathodically polarized steel wire mesh (inner ring). The outer ring is wired as the anode.

(0.011 to 0.323 mA/sq cm) between the electrodes is required. Because aragonite possesses higher strength than brucite, it was concluded that it is desirable to have a high aragonite-to-brucite ratio in the deposit for structural applications.[2]

Hilbertz also reported that current densities of less than 0.108 mA/sq cm resulted in high aragonite-to-brucite ratios.[2] This is likely because aragonite is precipitated at a pH only slightly above that of the surrounding water, and the brucite is precipitated at higher pH.[3] And, since high current density results in high reaction rates for reactions 1 and 2, which in turn raises the pH, it follows that relatively strong deposits should be obtained at low current densities. In fact, a similar observation was made much earlier by Humble, who noted that the deposits obtained at low current densities were more permanent.[4]

Therefore, it has been suggested by Hilbertz that this accretion process has potential applications in the building of marine structures such as artificial reefs, platforms, piling, and risers.[2] We believe that with the exception of building artificial reefs, this is too optimistic. However, in our opinion, a more realistic potential application of the accretion process would be to seal or fill cracks in marine concrete piles with the deposits. This process could be effected by securing a suitable anode material around and at a suitable distance from a pile and then applying direct current between this anode and the reinforcing steel in the pile, which would act as the cathode. If minor cracks in marine piles can be effectively sealed by the accreted minerals before they become serious, it would prevent the corrosion of the steel for some period of time. Therefore, this study was undertaken to evaluate the feasibility of applying the electrochemical accretion process as an alternative procedure for sealing cracks in marine concrete piles.

OBJECTIVES

The objectives of this study were: (1) to demonstrate that the electrochemical accretion process can be utilized to seal cracks in reinforced concrete and (2) to determine whether the process can seal cracks completely and improve the integrity of cracked reinforced concrete.

EXPERIMENTAL METHODOLOGY

Preparation of the Specimens

Two sets of cracked concrete specimens were utilized in this investigation. The set of smaller reinforced concrete specimens (see Figure 2) was fabricated with class A4 concrete[5] with wire mesh as reinforcement. Before the fresh concrete set, a groove (3-mm deep) was introduced on one face of each specimen at the center. (The groove focused the area of stress, so that when each specimen was loaded on the opposite face, a crack would form only on the grooved face of the specimen. This was an attempt to simulate typical cracks found on marine concrete piles.)

The specimens were then cured in a moisture room for a month, after which each specimen was stressed very slowly until a crack formed along the groove without completely splitting the specimen (see Figure 3). (The cracks introduced on these specimens were reasonably uniform in dimension, which ranged from 0.25 to 0.30 mm at the widest point to about 0.08 mm at the ends; however, the direction of the crack into the specimens varied from 0 to 2 mm away from the side of the center wire.) Afterward, the protruding section of the wire, with the exception of its tip, was coated with epoxy to eliminate any exposed wire that would short the direct current to the seawater surrounding the specimen.

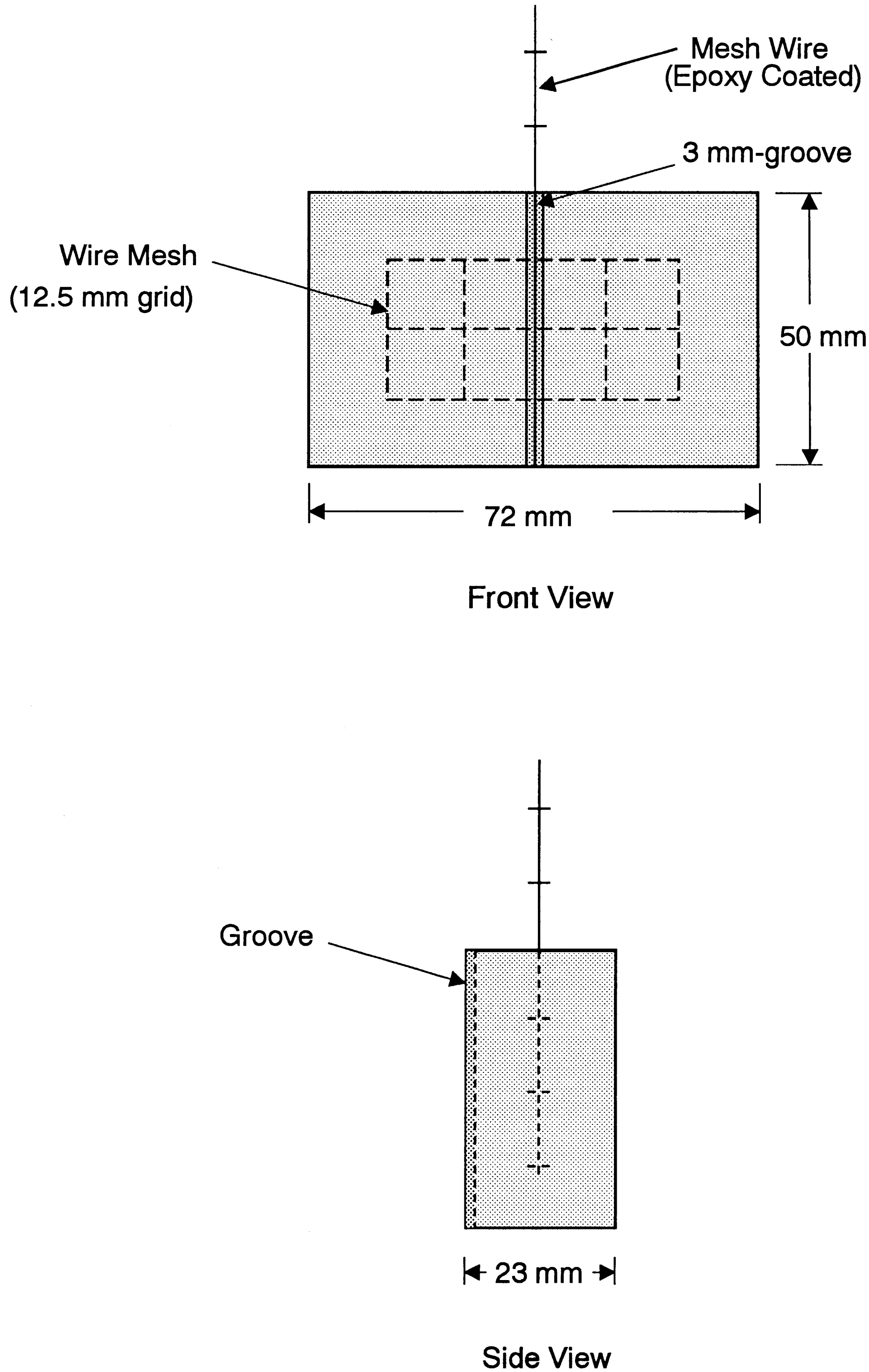


Figure 2. Wire mesh reinforced concrete specimen.

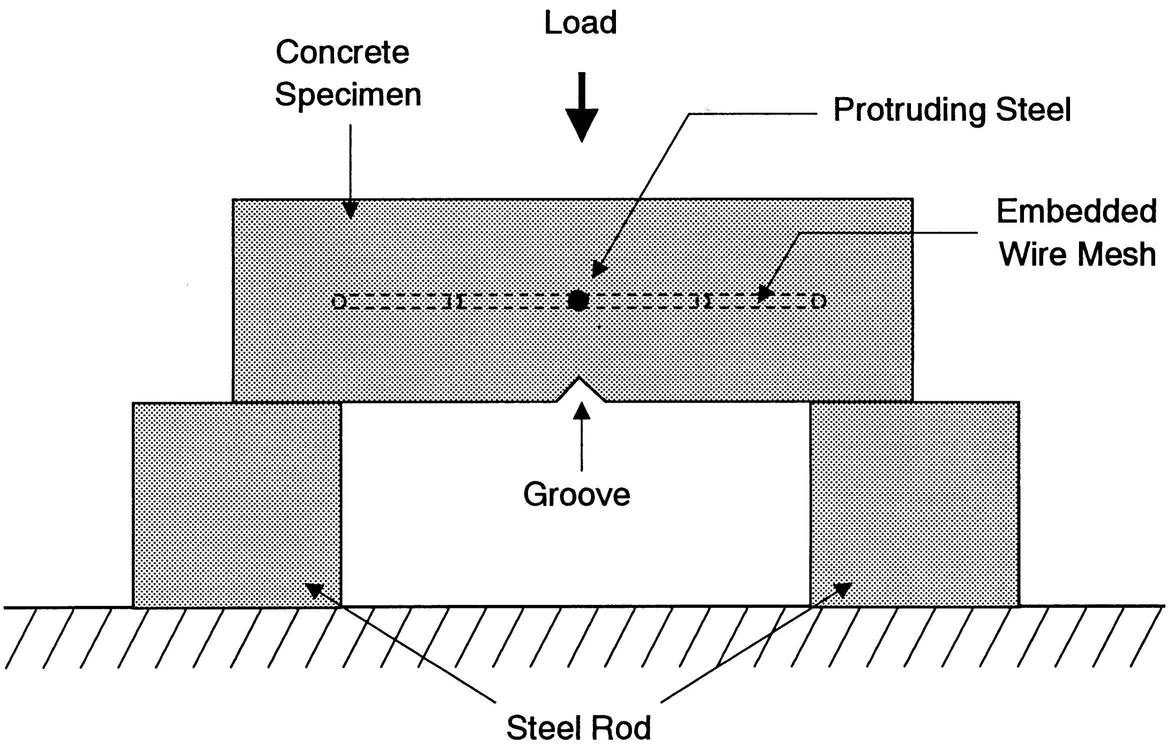


Figure 3. Setup for applying load on the concrete specimen to induce a crack along the groove.

The second set of larger reinforced concrete specimens (see Figure 4) were fabricated with No. 3 rebars and class A4 concrete mixture.[5] With these specimens, a 5-mm deep groove was also introduced on one face directly above the rebar before the fresh concrete set. After allowing the concrete to cure in a moisture room for a month, each specimen was stressed slowly (using the same setup illustrated in Figure 3) until a crack started to form at the groove. (The cracks introduced into these specimens were also reasonably uniform in dimension. They ranged from 0.30 to 0.33 at the widest point to about 0.08 mm at the ends. The direction of the crack in the specimens was also reasonably uniform, i.e., running toward the encased rebars.) The protruding section of the rebar in each specimen was then coated with epoxy.

Accretion Procedure

To effect accretion of minerals in the cracks, the concrete specimens were submerged in seawater (see Figure 5). For anodes, 3-mm (O.D.) titanium rods coated with a proprietary catalyst were selected over other anode materials (such as lead, graphite, platinum, and gold) for use in this investigation. A titanium anode rod, which was either 10 cm or 18 cm in length (depending on the

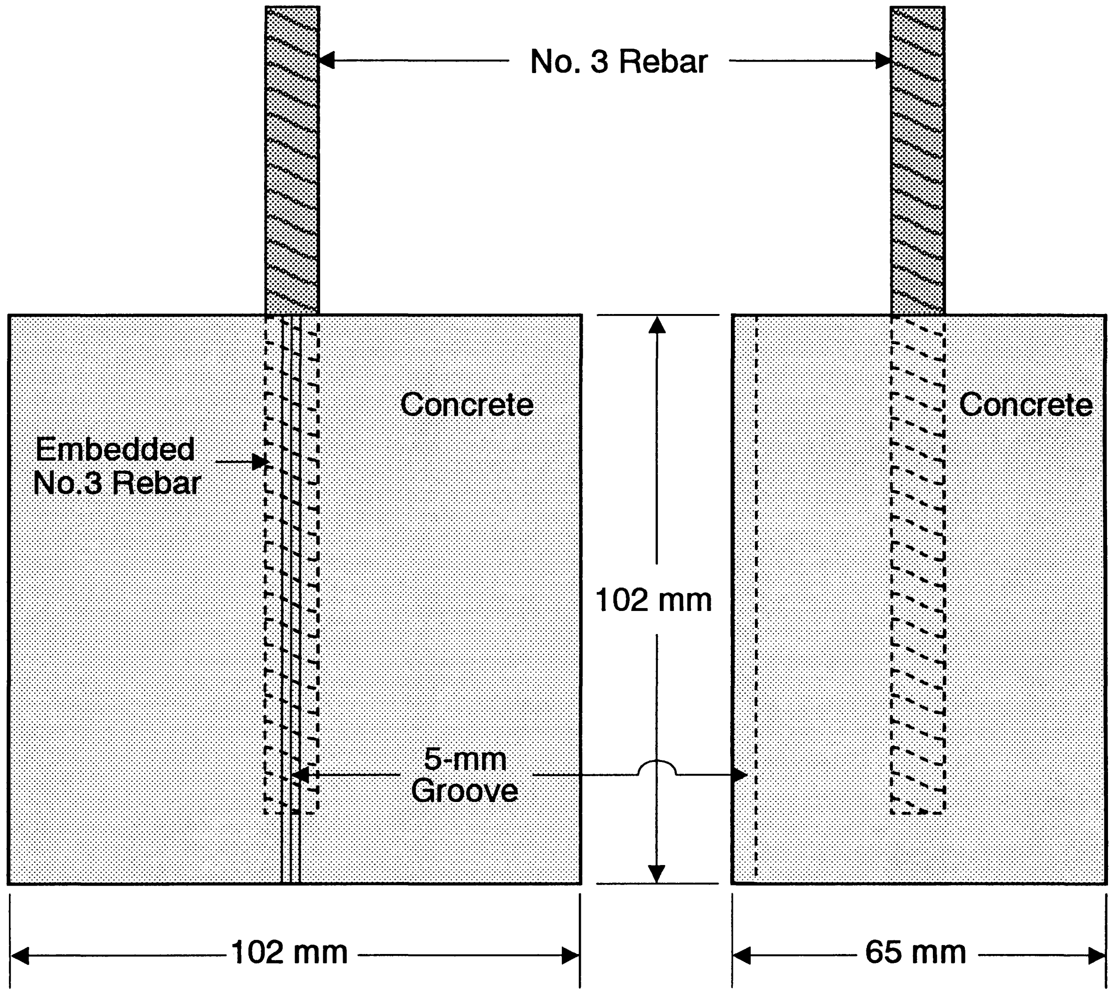
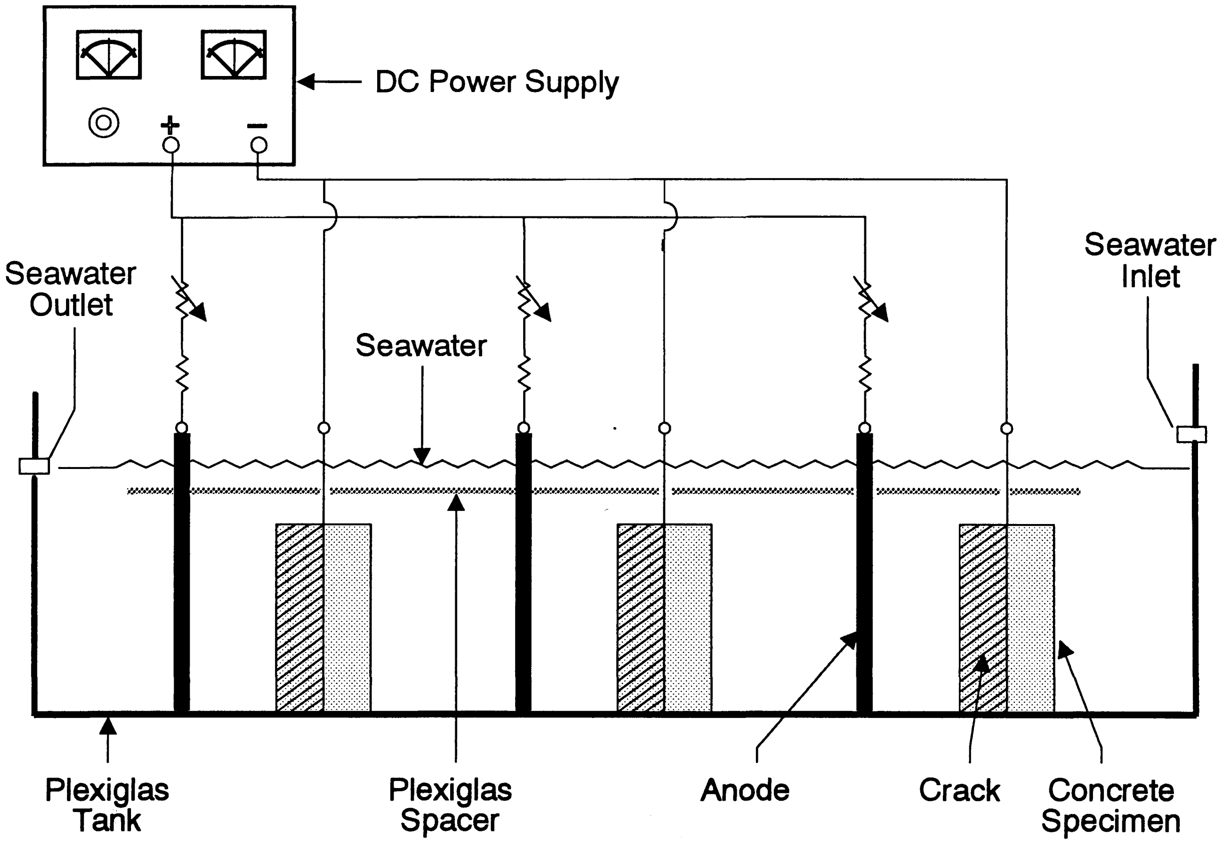


Figure 4. Rebar-reinforced concrete specimen.

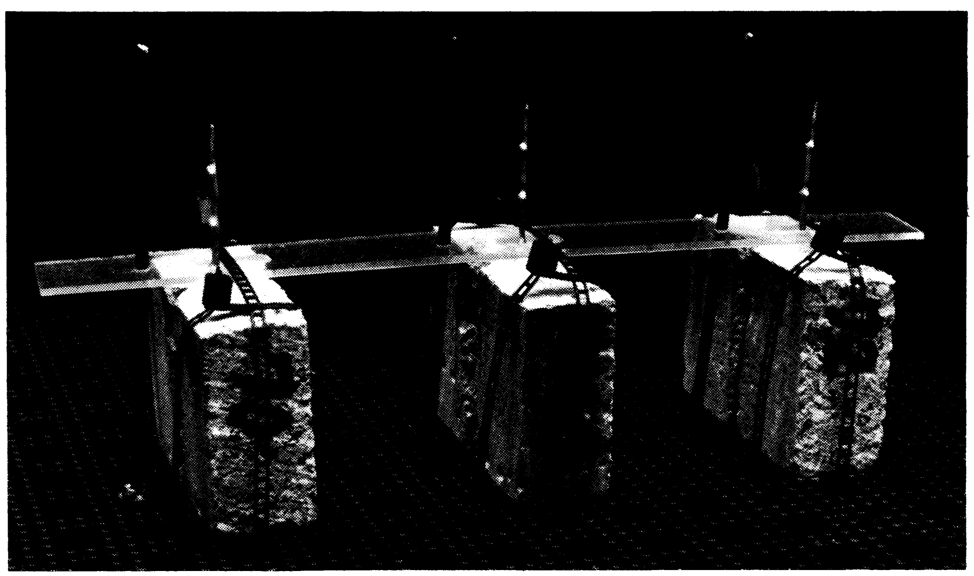
height of the concrete specimen), was secured approximately 15 mm in front of each concrete specimen directly opposite the crack. Then, the embedded steel mesh or rebar in each specimen was connected (by its exposed end) to the negative output terminal of a DC power supply, and the anode rod was connected to the positive output terminal through two resistors. All electrical connections between the power supply, the electrodes, and the resistors were made with No. 14 AWG-stranded copper wires. The concrete specimens were then negatively polarized at various current levels and for various accretion periods that ranged from 1 to 3 weeks.

Examination of the Specimens

Two nondestructive inspection techniques were utilized to examine the cracked reinforced concrete specimens in order to determine whether cracks



(a)



(b)

Figure 5. Setup used for accretion of seawater minerals in cracks in concrete specimens.

were being completely sealed. These techniques were neutron radiography and the measurement of ultrasonic pulse velocity (UPV), each of which was used on the cracked concrete specimens before and after the accretion process commenced.

The basic principle of x-ray or neutron radiography is that the transmission of this high-energy radiation through the object or material being examined is indirectly proportional to the density of the material. Therefore, if voids or cracks are present in any portion of the object, this portion would allow relatively higher transmission of these radiations than the rest of the object, and this variation in transmission across the object can be easily recorded by the use of films. Unfortunately, there is a limitation to the thickness of the concrete to which this technique can be applied. Therefore, the small specimens shown in Figure 2 were fabricated and accreted to allow the use of neutron radiography, which was performed using the 2-megawatt nuclear reactor at the University of Virginia in Charlottesville as the neutron source. To allow the crack in each specimen to be examined thoroughly, the radiography was performed on each specimen with the neutron beam aligned parallel to the axis of the crack in the specimen and then reoriented so that the beam was perpendicular to the crack (see Figure 6).

Because neutron radiography allowed the use of only the small specimens, which may not be representative of the concrete piles that the application of accretion would be intended for, the nondestructive inspection technique of UPV measurements was also used in this investigation. Even though the latter is probably comparatively less sensitive than radiography for crack detection, it allows the use of the larger specimens shown in Figure 4. Such measurements have been used on concrete to detect the presence of defects; therefore, they should provide useful information on the effectiveness of the accretion process in completely sealing cracks in reinforced concrete and in improving the integrity of such concrete. These measurements were conducted on each specimen before and after accretion using a UPV meter and a pair of 54 KHz transducers (see Figure 7). After accretion, each specimen was allowed to dry thoroughly before UPV measurements were conducted on the specimen.

RESULTS AND DISCUSSION

The accretion process was conducted at three different levels of direct current (1.0, 2.0, and 3.0 uA/sq mm) and for three different lengths of time (1, 2, and 3 weeks). During the accretion, the driving voltage in each circuit and the temperature and pH of the seawater in the middle of the tank were monitored weekly. The temperature was observed to vary between 18 to 27^{o}C (65 to 81 ^{o}F), and the pH fluctuated between 8.0 and 8.1.

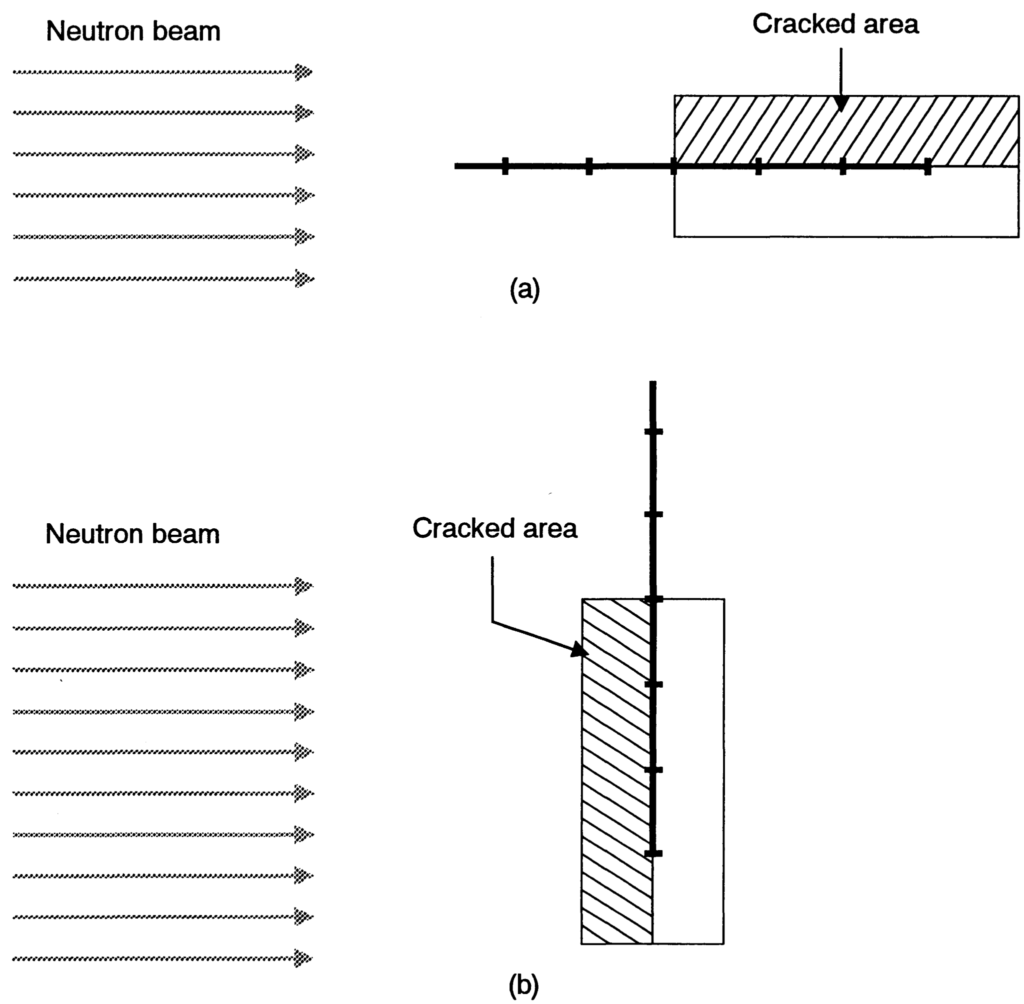


Figure 6. Alignments of the small concrete specimens against the neutron beam during radiography.

At the beginning of each series of accretions, the driving voltages from the power supplies varied between 1.18 to 2.73 volts depending on the desired current levels. After the first week of accretion, these driving voltages increased by approximately 3 to 10 percent in order to maintain the respective selected current levels. After the second week, the observed increases in the driving voltage were generally less than 0.2 percent. Increases in the driving voltage necessary to maintain a certain level of accretion current across the specimens with increased accretion time are consistent with the observed growth of the accretion products in the specimen.

In most cases, it took approximately 3 days after the beginning of the accretion process for the mineral deposits to appear in the cracks. This was even true for the specimens subjected to the lowest current level. Thereafter, the deposits started to grow out of the cracks. As would be expected, the amount of

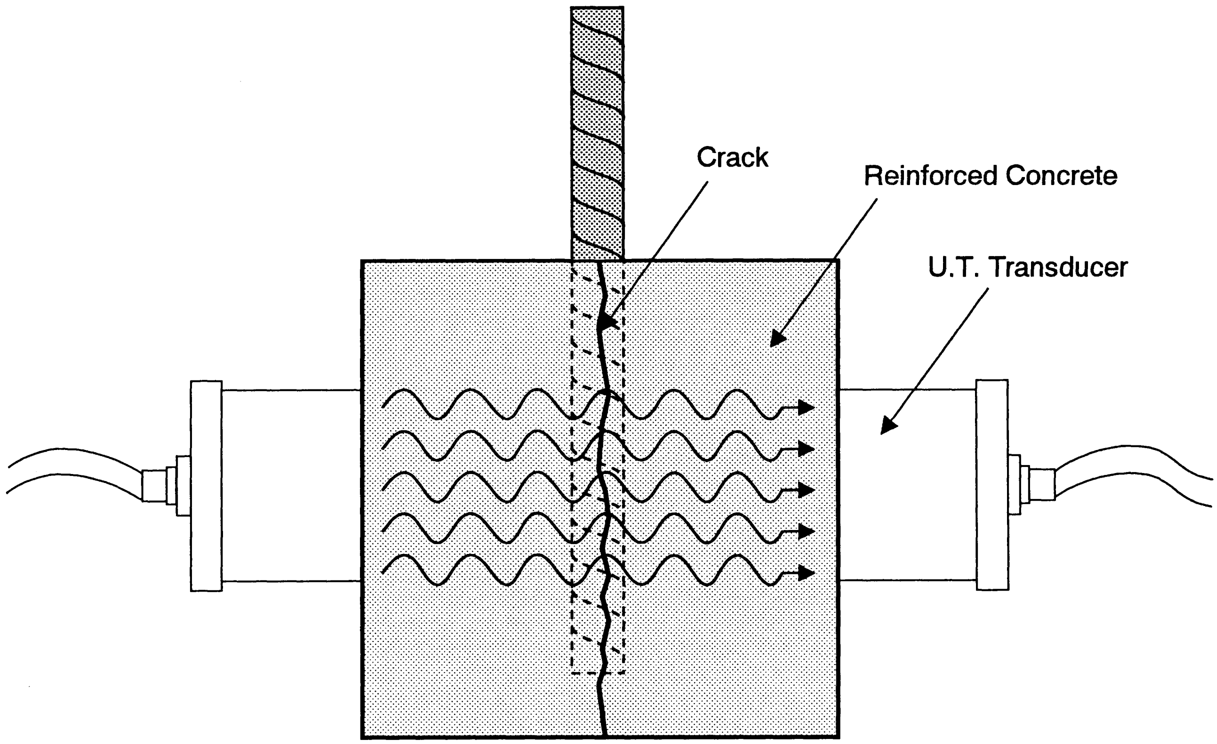


Figure 7. Measurement of UPV through the concrete specimen.

accretion in each specimen was directly dependent on the current level and the accretion time. The deposits eventually extended into the immediate surrounding of the mouth of the crack (see Figure 8) after approximately 1 week of accretion. This pattern of growth in the deposits was observed for both groups of specimens.

The deposits of minerals in the cracks and in the pores of the concrete prevent the easy access of water into the concrete specimens, which leads to increases in the electrical resistance of the specimens. Such increases in the resistance of the specimens would account for the observed increases in the driving voltage from the power supply that was discussed above.

To estimate the amount of deposits obtained in the small specimens, the dry weight of each of these specimens was measured before and after the accretion. The amount of accumulated deposits that were observed in these specimens (as a function of the accretion current and time) are shown in Table 1 and plotted in Figure 9. It is evident that the amount of deposits found in the specimens was directly influenced by the accretion current, especially after the first week of accretion. Furthermore, for the series of specimens subjected to an accretion current of 1.0 uA/sq mm (of the reinforcement), there was a discernible pattern of increase in the amount of deposits with increased accretion time. However, amongst the specimens subjected to the higher levels of accretion cur-

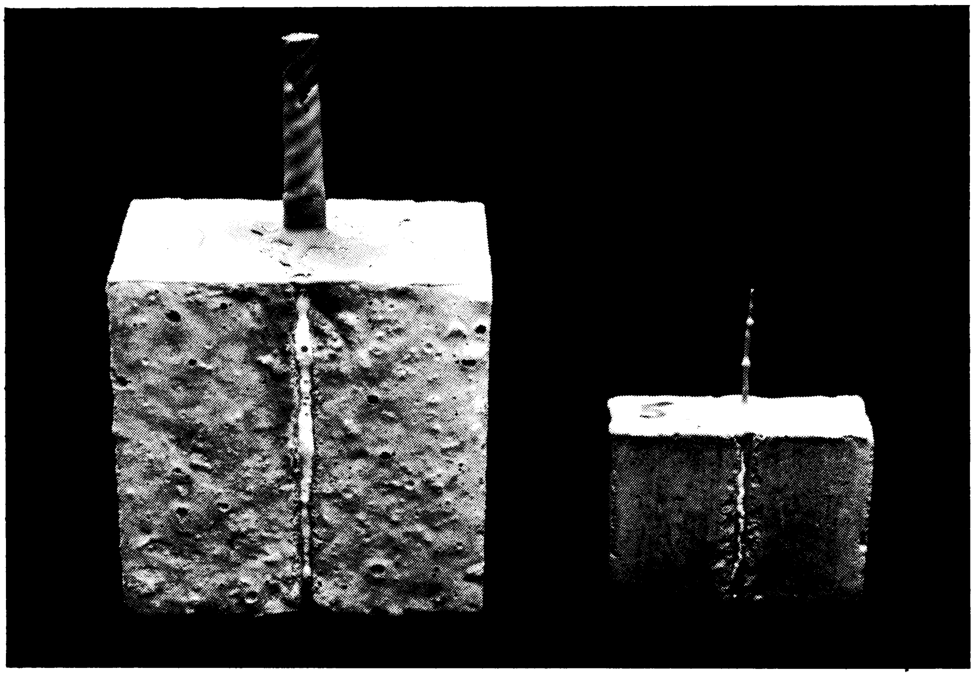


Figure 8. Reinforced concrete specimens with cracks sealed with accreted seawater minerals.

rents (2.0 and 3.0 uA/sq mm), this trend was not as evident. This lack of a clear trend of increasing deposits with increasing accretion time at the higher accretion currents very likely shows that applying the lowest accretion current level of 1.0 uA/sq mm for one week almost produced a sufficient amount of mineral deposits to fill the crack in each specimen. It is suspected that the reversed trend observed in some of the specimens that were subjected to longer accretion times was merely an aberration probably resulting from the narrower cracks in those specimens.

Neutron Radiographic Examination of Accreted Specimens

Figure 10 shows two sets of neutron radiographs of one of the small specimens that were obtained before and after accretion to demonstrate the suitability of neutron radiography for detecting cracks in concrete specimens. Careful comparison of these radiographs shows that it is not difficult to distinguish the unfilled crack in the specimen before accretion from the filled crack after accretion.

To allow some sort of quantitative determination of the extent to which the crack in each specimen was sealed by the accretion deposits by comparison of the radiographs obtained before and after accretion, it was necessary to

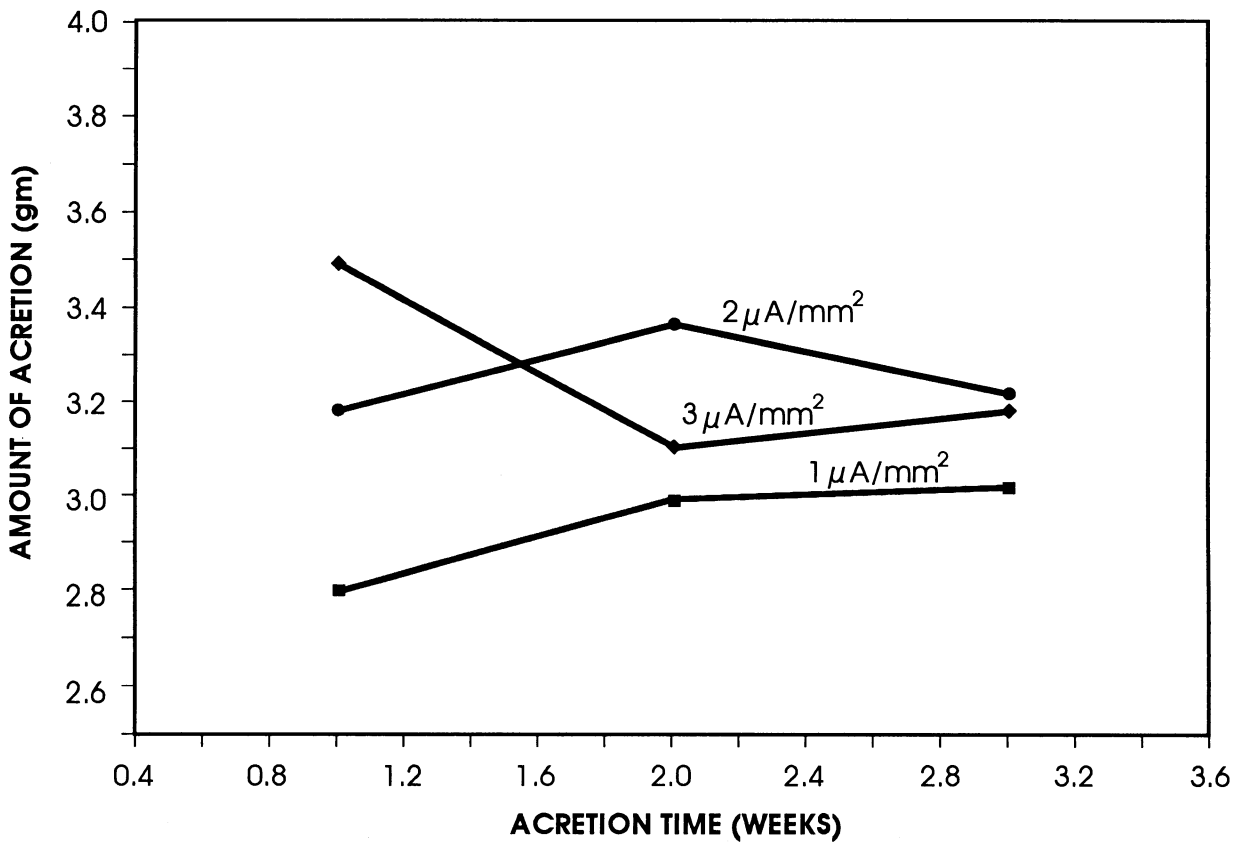
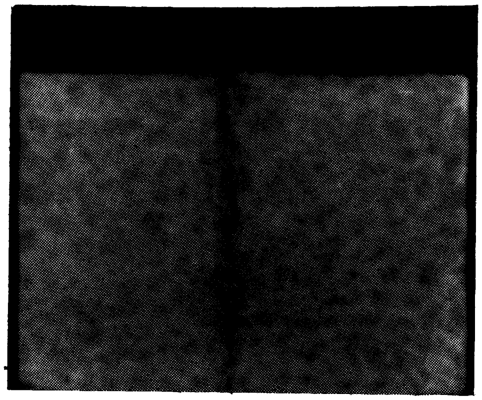


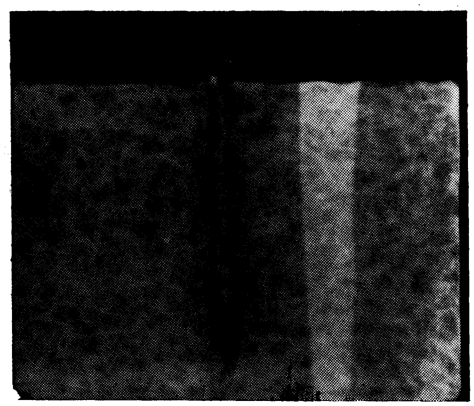
Figure 9. Influence of accretion current and time on the amount of accretion deposit.

devise a scale of 1 to 10: 1 for 0 percent and 10 for 100 percent of the crack sealed. This improvisation was necessary because there is no proven method for quantifying defects such as cracks and voids manifested in the radiographs of any materials being inspected. (In comparison to other nondestructive inspection techniques, neutron radiography is still in its infancy and is qualitative in nature, especially when it comes to the inspection of concrete.) By examining the radiographs for each specimen and using this rating scale, the effectiveness of the electrochemical accretion process as a function of accretion current and time was assessed.

The results of this assessment are presented in Table 2. These data show that for the specimens subjected to 1.0 uA/sq mm of accretion for one week, only approximately 90 percent of each crack in the specimens was sealed by accretion deposits, and a longer accretion time did not yield any improvement. It is also evident that the use of accretion current beyond 1.0 uA/sq mm did not

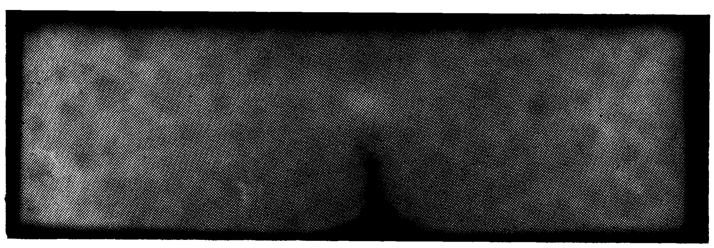


Before



After

(a)



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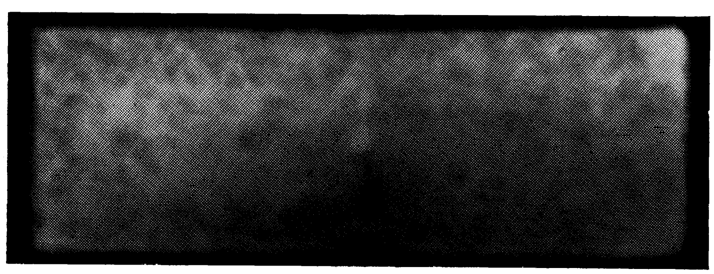

After

(b)

Figure 10. Neutron radiographs of specimens before and after accretion.

Table 1
INFLUENCE OF ACCRETION CURRENT AND TIME
ON THE AMOUNT OF ACCRETION

Specimen	Accretion Current (uA/sq mm)	Accretion Time (Week	Specimen Weight Before	Specimen Weight After	Weight of Deposit (gm)	Average (gm)
7	1.0	1	195.90	198.65	2.75	2.80
8			211.34	214.15	2.81	
9			201.73	204.58	2.85	
10	1.0	2	199.42	202.12	2.70	2.99
11			185.64	188.90	3.26	
12			193.53	196.55	3.02	
13	1.0	3	197.29	200.25	2.96	3.01
14			190.10	193.05	2.95	
15			200.62	203.75	3.13	
16	2.0	1	191.21	194.40	3.19	3.18
17			190.18	193.10	2.92	
18			202.33	205.77	3.44	
19	2.0	2	185.38	188.33	2.95	3.36
20			189.71	193.30	3.59	
21			200.21	203.74	3.53	
22	2.0	3	202.88	205.97	3.09	3.21
23			193.91	197.14	3.23	
24			209.83	213.15	3.32	
25	3.0	1	208.39	212.34	3.95	3.49
26			208.39	211.58	3.19	
27			203.82	207.15	3.33	
28	3.0	2	190.62	193.46	3.06	3.10
29			204.58	207.80	3.22	
30			183.22	186.24	3.02	
31	3.0	3	203.17	206.27	3.10	3.17
32			210.34	213.66	3.32	
33			209.71	212.81	3.10	

improve the effectiveness of the sealing. On the contrary, these data showed that higher current levels may actually interfere with the complete sealing of the cracks (possibly by causing rapid deposition of minerals at the mouth of a crack and thereby preventing further accretion inside the resulting cavity by restricting access of additional seawater into the crack). Ideally, the accretion of deposits should begin slowly at the very inside edge of a crack and then grow slowly out toward the mouth of the crack. The data also showed that perhaps an accre-

Table 2
INFLUENCE OF ACCRETION PARAMETERS ON THE EXTENT OF CRACKS SEALED BY DEPOSITS (AS DETERMINED BY RADIOGRAPHY OF SPECIMENS)

	Accretion		Extent of Crack Filled[a] —Specimen Radiographed From			
Specimen	Current (uA/sq mm)	Time (Week)	Front	Top	Total Rating	Average Total Rating
7	1.0	1	8	10	18	18
8			8	8	16	
9			10	9	19	
10	1.0	2	9	8	17	17
11			9	8	17	
12			9	8	17	
13	1.0	3	9	8	17	16
14			9	6	15	
15			8	9	17	
16	2.0	1	9	9	18	18
17			9	9	18	
18			9	8	17	
19	2.0	2	9	9	18	17
20			9	8	17	
21			8	7	15	
22	2.0	3	9	8	17	17
23			9	9	18	
24			8	8	16	
25	3.0	1	7	8	15	16
26			9	9	18	
27			7	9	16	
28	3.0	2	9	7	16	15
29			8	6	14	
30			8	8	16	
31	3.0	3	8	8	16	15
32			7	8	15	
33			8	7	15	

a. On a scale of 1 to 10: 1 is none of the cracks were sealed; 10 is cracks were completely sealed.

tion current level significantly lower than 1.0 uA/sq mm would likely yield near complete (perhaps complete) sealing of the cracks in the specimens tested.

It is not known to what extent the cracks in a reinforced concrete pile have to be sealed. For completely restoring a pile, a 100 percent seal may be necessary; however, for preventing further damage, the degree of sealing that was observed with the test specimens may be more than sufficient.

Examination of the Specimens with UPV Measurements

As described earlier, the UPV of the larger cracked concrete specimens were measured before and after they were subjected to the electrochemical accretion process. Table 3 presents the results of these measurements. As expected, the accretion of mineral deposits in the crack in each specimen tested increased the UPV of the concrete. The average increase in UPV ranged from 10.8 to 14.8 percent, which indicates some improvement in the integrity of

Table 3
ULTRASONIC-PULSE VELOCITY OF CRACKED CONCRETE SPECIMENS
BEFORE AND AFTER ACCRETION

Specimen	Current (uA/sq mm)	Time (week)	UPV (m/sec) Before Accretion	UPV (m/sec) After Accretion	Change (percent)	Average Change (percent)
G3 G4	1.0	1	3360 3260	3790 3810	12.8 16.9	14.8
G5 G6	1.0	2	3750 3410	4160 3880	10.9 13.8	12.4
G7 G8	1.0	3	3330 3340	3670 3740	10.2 12.0	11.1
G9 G10	2.0	1	3180 3420	3710 3790	16.7 10.8	13.7
G11 G12	2.0	2	3300 3310	3710 3680	12.4 11.2	11.8
G13 G14	2.0	3	3460 3320	3860 3830	11.6 15.4	13.5
G15 G16	3.0	1	3680 3150	3980 3570	8.2 13.3	10.7
G17 G18	3.0	2	3280 3260	3710 3710	13.1 13.3	13.5
G19 G20	3.0	3	3410 3390	3830 3780	12.3 11.5	11.9
		Average	3370	3790	12.6	

these reinforced concrete specimens. Amongst the various combinations of accretion current levels and times tested, it appeared that the best improvement was provided by the lowest accretion current used (1.0 uA/sq mm) with an accretion time of one week. Furthermore, neither the use of a longer accretion time nor a higher accretion current appeared to provide better results.

It is not possible to make any statement about the improvement in the strength of the concrete specimens from the accretion-induced increase in the UPV other than that the process afforded some improvement in their structural stiffness.

Overall, these results appeared to show that even the lowest accretion current of 1.0 uA/sq mm is more than that needed to effect the ideally slow accretion of deposits from the inner end of a crack. This current level and those that were higher appeared to induce "flash" precipitation of the minerals at a less than ideal location inside the cracks. Again, perhaps an accretion current significantly lower than 1.0 uA/sq mm would have likely yielded closer to complete (and perhaps complete) sealing of the cracks in the specimens tested.

Finally, it is worthwhile to reiterate that although it may be desirable to be able to completely seal all the cracks in a concrete pile, it may be unnecessary, i. e., near complete sealing may be sufficient enough to ensure long service life especially if the reinforcement surfaces are coated with the deposits. In fact, Humble[4] established that if the deposits on the metal surfaces are hard and continuous, they provide considerable protection for the encased metal, presumably because the deposits coat the metal surface and restrict access of oxygen, which is essential to corrosion.

The lowest accretion current used in this study is, in fact, approximately a hundred times that of the direct current found necessary to cathodically protect the reinforcement in concrete bridges, which is typically 0.01 to 0.02 uA/sq mm.[6] Consequently, we predict that if an accretion current of this very low level is applied in an actual concrete pile in a marine environment, not only would all existing cracks in the pile be sealed completely, but the reinforcement would also be cathodically protected from any corrosion. This low-level current would not only cathodically polarize the reinforcement but would also seal the cracks and the pores in the concrete, thereby restricting the ingress of seawater and oxygen into the piles, which are ingredients necessary for corrosion to occur. It is estimated that the electrical power that would be needed to effect these measures on a pile would be only approximately 0.2 watt, which is considerably lower than that required for a light bulb. Since this electrical power is extremely small, the resulting benefits of these double measures to extending the service life of such piles would undoubtedly be significant.

CONCLUSIONS

1. The electrochemical accretion process can be utilized to seal undesirable cracks in concrete piles located in marine environments.

2. The levels of accretion current used in the study were too high; consequently, accretion occurred too rapidly and at the wrong locations inside the cracks. This resulted in incomplete sealing of the cracks in the specimens tested. However, it is not known whether complete sealing of each crack in a pile is absolutely necessary in actual application.

3. The results showed that considerably lower levels of current would be preferable to achieve the desirable slow accretion of deposits from the very inside end of each crack. This ideal accretion current level may not be too different from the current level that is typically required to cathodically protect steel in concrete structures.

RECOMMENDATIONS

Since the ideal accretion current is likely to be not much different from that which would be needed to cathodically protect the concrete piles in the Hampton Area for the protection of which the application of the accretion process is intended, it is unlikely that further study to provide better understanding of the crack sealing process would provide any significant benefit, unless an adverse effect associated with the process is later uncovered, which is extremely unlikely. Furthermore, since it is likely that cathodic protection will eventually be necessary to halt steel corrosion in these piles, the accretion process and its beneficial effects will automatically occur.

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