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The Effects of Latex Additions on Centrifugally Cast Concrete for Internal Pipeline Protection

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Abstract

Centrifugally-cast concrete liners applied to the interiors of plain steel pipe sections were tested for corrosion performance in brine solutions. An American Petroleum Institute (API) standard concrete, with and without additions of a styrene-butadiene copolymer latex, was subjected to simulated service and laboratory tests. Simulated service tests used a mechanically pumped test manifold containing sections of concrete-lined pipe. Linear polarization probes embedded at steel-concrete interfaces tracked corrosion rates of these samples as a function of exposure time. Laboratory tests used electrochemical impedance spectroscopy to study corrosion occurring at the steel-concrete interfaces. Electron probe microanalysis (EPMA) determined ingress and distribution of damaging species, such as Cl, in concrete liners periodically returned from the field. Observations of concrete-liner fabrication indicate that latex loading levels were difficult to control in the centrifugal-casting process. Overall, test results indicate that latex additions do not impart significant improvements to the performance of centrifugally cast liners and may even be detrimental. Corrosion at steel-concrete interfaces appears to be localized and the area fraction of corroding interfaces can be greater in latex-modified concretes than in API baseline material. EPMA shows higher interfacial Cl concentration in the latex-modified concretes than in the API standard due to rapid brine transport through cracks to the steel surface.

Key terms: concrete, corrosion, concrete lined steel pipe, electrochemical impedance spectroscopy.

Introduction

The U.S. Strategic Petroleum Reserve (SPR) stores upwards of 500 million barrels of crude oil in caverns formed in naturally occurring underground salt domes situated along the Gulf Coast of Louisiana and Texas. The majority of these storage caverns have been formed by a solution mining process that uses low salinity water, usually from a nearby intracoastal source. This water is injected into the dome in a controlled fashion, dissolving away the salt to form a storage cavern with the desired dimensions. This solution mining process generates large quantities of brine that is transported through 0.91 to 1.07 m (36 to 42 in.) diameter steel pipelines to diffusers located in the Gulf of Mexico, or to disposal wells in sandy, porous formations near the storage site. At sites where solution mining has been completed, the brine disposal pipelines must be used on a periodic basis to accommodate normal site activities. Currently, the SPR operates approximately 65 miles of these brine disposal pipelines[1].

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Over the 15 year history of the SPR, the brine disposal pipelines have, in certain instances, experienced aggressive erosion and corrosion damage. To combat erosion and corrosion damage, internal cement linings on the steel pipe are being considered as a replacement strategy to offer extended service life and lower pipeline maintenance costs. Concrete liners are expected to provide a buffer against erosion damage and provide corrosion protection by passivation of the steel in the high pH cement paste.

Latex additions to concrete are reported to improve concrete properties important in the SPR application including durability, adhesive properties, resistance to chloride ingress, shear bond strength, and tensile strength[2]. Because of the potential for improvements in concrete properties, latex modified concretes are candidate liner materials.

Currently, the performance of a variety of industrial standard and experimental concrete compositions for use in SPR brine disposal pipelines are being explored. In this paper, interim results are reported from on-going studies involving an American Petroleum Institute (API) standard cement consisting of 60% high sulfate resistance Portland Cement with 40% silica fume fly ash and this API standard concrete modified by additions of a styrene-butadiene copolymer latex emulsion. The performance of these concrete liners has been evaluated in a testing manifold using actual brine generated at an SPR site. Additional specimens have been subjected to SPR brine under non-flowing conditions, and have been returned to the laboratory at regular intervals to analyze brine penetration and concrete deterioration as a function of exposure time. Laboratory scale specimens have also been constructed so that the concrete liners can be evaluated using electrochemical impedance spectroscopy.

Experimental Procedures

Materials and Specimen Preparation. Concrete lined steel pipe specimens were prepared using commercially available materials. Plain carbon steel pipe sections 5.8 to 6.8 m (19 to 22 ft) in length with a 76 mm (3 inch) inner diameter were prepared for lining by sandblasting the pipe interior. The baseline concrete mixture consisted of 60% (by weight) API Class C (0% C_3A) high sulfate resistance Portland cement, and 40% API Class F (<10% CaO, 5 -10% C) fly ash[2]. Latex additions of 5%, 10%, and 15% by weight were made by adding a styrene-butadiene copolymer emulsified in water to the concrete mix prior to application in pipe sections. The emulsion contained approximately 50% solids by weight. Table 1 lists the amounts of the above ingredients used to make the baseline and latex modified concretes.

The concrete lined pipe was fabricated at Permian Enterprises, Odessa, TX using their standard centrifugal casting production methods. The concretes were prepared in a mixing bin then pumped through a delivery lance into the pipe section to be lined. For the latex modified concretes, the emulsion was added directly to the mixing bin without any other alterations in the standard fabrication process. The pipe section was capped at one end and the concrete was pumped at a predetermined rate through the lance as it was withdrawn. After charging the pipe section, the remaining end of the pipe was capped and the section was loaded onto rollers for the spinning operation. Pipe sections were spun at speeds ranging from 12.7 m/s (2500 ft/min) to 14.2 m/s (2800 ft/min) for 1.5 to 4 minutes generating forces in excess of 20 g. After spinning, the pipe section was removed from the rollers, the ends were uncapped and excess water and latex were drained from the pipe. The fact that latex was observed in the run-off when pipe sections were drained indicated that not all the latex was retained in the liner. Pipe section ends were then recapped and kiln cured at 65^{o} C for approximately 18 hours. Full details of the centrifugal casting process can be found in reference 4.

Liner thicknesses and densities are listed in Table 1. Densities were determined using a high precision balance to determine mass, and gas pyncnometry to determine volume. The densities for the latex modified concretes are lower than the baseline concrete indicating that latex was incorporated into the liner. However, the densities for all three latex loading levels were nearly identical suggesting that the amount of latex retained after centrifugal casting was similar. In spite of this apparent similarity, the latex modified concretes performed quite differently in corrosion experiments and are referred to according to their intended loading levels (5%, 10%, and 15%) throughout the remainder of the text.

On-site Simulated Service Testing. A scaled test system was constructed at the Big Hill SPR Site in Winnie, TX. This test was performed to measure the concrete liner durability and pipe corrosion rate using actual brine generated from normal site operations. The advantages of this test was that real service environments were encountered, and test results were quickly interpreted. The primary disadvantages were that brine concentrations varied during the test period compromising experimental control, and the emergence of performance trends was slow since this was not an accelerated test.

Concrete lined test pipes were placed into a manifold through which site brine was mechanically pumped. Brine was withdrawn from a settling ponds, pumped through the system and deposited back into the settling pond at a distance removed from the system intake (approximately 20 m). The flow rate through the 5.0 cm (2 in.) inner diameter piping used in the manifold was selected to generate a pipe wall shear stress equal to that of a 0.91 m (36 in.) pipe carrying brine flowing at 2.36 m/s (7.75 ft/s). Corrosion rates were measured using a linear polarization probes fitted into diametrically opposing ports in the pipe section prior to the concrete lining operation. Instantaneous corrosion rate measurements were made by determining the polarization resistance using a 10 mV voltage perturbation about the free corrosion potential. Corrosion rates were determined from the polarization resistance using the Stearn-Geary equation[5] assuming a value of 25 mV for B where $B = \beta_a\beta_c/2.3(\beta_a + \beta_c)$, with βa and βc representing the anodic and cathodic Tafel slopes. The appropriateness of the linear polarization method for these tests is discussed in the 'Results' section.

Electrochemical Impedance Spectroscopy (EIS). To supplement on-site testing, laboratory-based EIS was performed on cells constructed from concrete lined pipe sections. Test specimens, 100 mm in length, were cut from pipe sections and sealed with rigid plastic at one end. Specimens were placed on end and filled with air sparged saturated solution consisting of 300 g/l NaCl, 4.0 g/l $CaSO_4$, and 1.0 g/l $MgCl_2$, which approximated saturated SPR brine[6]. Air sparging kept the dissolved oxygen concentration constant near its saturation value of 2 ppm[6], while the use of a saturated solution insured that composition variations were minimized during the lengthy tests.

EIS experiments were made using a two electrode measurement, where the working electrode was the steel pipe and the counter electrode was a cylindrical nichrome mesh inserted into the cell symmetrically about the pipe centerline. The EIS measurement systems consisted of either a PAR 273 potentiostat/Solartron 1250 frequency response analyzer (FRA) combination, or a Solartron 1286 electrochemical interface/1255 FRA combination. Each system was controlled by Scribner Associates' Z plot impedance software package installed on an IBM personal computer. Typically, measurements were made at frequencies ranging from 65 kHz to 1 mHz by sampling at 10 points per decade frequency using a 20 mV sinusoidal voltage perturbation. At any frequency, the measured current was integrated to minimize the effects of spurious components to the signal. EIS measurements were made at weekly intervals for the first 4 weeks, biweekly from 4 to 24 weeks, and monthly thereafter.

Electron Probe Microanalysis (EPMA). EPMA of the concrete liners was used to track ingress of brine and degradation of the cement liners as a function of exposure time. Specimens were exposed at the Big Hill SPR site and returned to the laboratory for analysis at regular intervals. Sections of liners were removed, potted in epoxy and polished with successively finer papers and diamond pastes until the surface was sufficiently smooth for X-ray microanalysis. X-ray linescans were performed using a JEOL 8600 electron microprobe. Analyses were conducted by stepping the beam in 50 μm increments from the steel-concrete interface to the concrete-brine interface. Quantitative wavelength dispersive X-ray data were generated using a 25 nA beam at an accelerating voltage of 15 keV. The data were corrected for fluorescence, atomic absorption, and atomic number using the Bence-Albee technique. All of the major elements in the system were measured, although the focus in this paper is on the distribution of Cl.

Results and Discussion

On-site Simulated Service Testing. Table 2 lists maximum corrosion rates detected at the steel-concrete interface over 314 days of test manifold operation. The steady state corrosion rate for bare steel in the test manifold is listed for comparison. No corrosion was detected at the linear polarization probes in the baseline concrete. Some indication for corrosion was found for the latex modified concretes, however. Overall, these values were small compared to the steady state corrosion rate determined for the bare steel control. The data in Table 2 were calculated using a B value of 25 mV, and were not corrected for iR drop occurring in the concrete. Accepted values for B are 26 mV for corroding steel, and 52 mV for passive steel[7], hence the value used here is comparatively low. Additionally, visual inspection of samples returned from the site showed that corrosion at the steel-concrete interface was localized. For these reasons, these data are taken only to indicate that concrete liners impart significant corrosion protection compared to unprotected steel, and to indicate the relative presence or absence of corrosion among the concrete lined specimens.

EIS. A complex plane plot representative of the response for both the baseline and latex modified concrete liners is shown in Figure 1. The inset shows the small arc or 'spur' observed at high frequencies. The low frequency arc was semicircular and depressed with respect to the real axis. The high frequency arc was not always fully resolved, but also appeared to be a depressed semicircle. Both arcs were consistently observed throughout the duration of the exposure period for both the baseline and latex modified concretes. The time constant for the high frequency arc was typically in the range of 10^{-3} to 10^{-4} s, while that for the low frequency arc was usually between 300 and 1000 s. The impedance response of these systems was interpreted using the equivalent circuit model (Figure 2a) developed by Macdonald[8] for corrosion of rebar in chloride-contaminated concrete. In this model, two parallel subcircuits are used to represent corroding and passivated regions of the steel cement interface. These parallel subcircuits are arranged in series with a concrete resistance, R_c. The subcircuit for the passivated area of the interface is comprised of a capacitance, C_{pa}, in parallel with a charge transfer resistance R_{pa}. The subcircuit for the corroding area of the interface is comprised of a capacitance, C_{ca}, in parallel with a charge transfer resistance, R_{ca}, and a diffusional impedance, Z_W. A_{pa} and A_{ca} in Figure 2a denote the passivated area fraction and the corroding area fraction respectively. Inspection of specimens returned from the field showed that corrosion at the steel-concrete interface was localized, indicating that this model was physically realistic for the present situation.

For complex nonlinear least squares (CNLS) fitting of the low frequency arc, a more generalized form of the model in Figure 2a was adopted. In the modified equivalent circuit shown in Figure 2b, the low frequency arc was modeled using a resistor in parallel with a constant phase element (CPE); a combination otherwise known as the ZARC impedance function[8]. As shown in Figures 3a and b, this equivalent circuit was capable of accurately fitting spectra from baseline and latex modified concrete lined pipe specimens. Good fits were regularly obtained even for long exposure times. The ZARC function is often used to model depressed arcs in the complex plane, so the level of agreement between the model and the data in Figures 3a and b is not surprising. The high frequency arc was not always fully resolved, and fitting was not performed. The Z' intercept of the low-frequency side of the arc was used for estimating R_{pa}.

The generalized model was used to reflect the fact that charge transfer and diffusional impedances were not clearly distinguished in the impedance response of these systems. Use of the ZARC function is appropriate for modeling systems where the relaxation time is not single valued but distributed about some mean value[9]. In concretes, the conductive pathways are the paste (Portland plus water), and shrinkage cracks filled with intruding brine. A multitude of these pathways exist in the liner with similar, though not identical relaxation times. Additionally, this and previous studies[10] suggest that the mean time constant for diffusional processes in the concrete, and the time constant due to charge transfer at a corroding steel-concrete interface are similar. Separating out the diffusional impedance is further complicated by the fact that good mass transport data are not readily available for concretes of the type under study here. The ZARC function used in the CNLS fitting allowed a lumped quantity, R_{ca}, to be determined without having to distinguish between diffusion and charge transfer components.

Figure 4 shows the measured charge transfer resistance associated with the passivated interface, $R_{pa}{}^{m}$, as a function of exposure time for the baseline and latex modified concretes. The measured resistance is given by:

$$R_{pa}{}^{m} = \rho_{pa}{}^{o} / A_{pa} \qquad \text{(eq. 1)}$$

where $\rho_{pa}{}^{o}$ is the area specific resistivity of the passive interface and, A_{pa} is the interfacial area. This equation illustrates the inverse relationship between the measured resistance and the passive interface area. Assuming $\rho_{pa}{}^{o}$ is similar for each type of concrete, Figure 5 indicates that the baseline material exhibits the largest passive interfacial area for exposure times up to 100 days. After this time, $R_{pa}{}^{m}$ for the 5% latex concrete appears to fall, suggesting that corroding interface is passivated. The 10% and 15% latex modified concretes exhibit high $R_{pa}{}^{m}$ presumably indicating smaller passive interface areas.

Figure 5 shows the charge transfer resistance of corroding areas as a function of exposure time. These data are highly scattered, but the general trend appears to be that largest R_{ca} values are exhibited for the latex modified concretes. The R_{ca} value plotted in Figure 5 includes a contribution due to diffusional impedance, Z_w, and evaluation of these data by the method used above is not believed to be valid due to intrinsic variations in Z_w caused by the latex additions.

EPMA. Figure 6a is a plot of chloride concentration as a function of position in the 5% latex modified concrete liner after 60 days exposure to brine at the SPR. This plot illustrates how brine is transported and partitioned in the concrete. The predominant feature of this plot is the high Cl concentration near the concrete-brine interface due to penetration of the brine through the paste. Away from this large Cl spike, smaller spikes are observed. These are due to shrinkage cracks in the concrete liner that filled with brine during exposure. These cracks appear to deliver brine to the steel-concrete interface because the Cl levels there are clearly elevated. Elevated Cl levels at the steel cement interface were observed after 30 days exposure to SPR site brine indicating that transport of brine through cracks is relatively rapid.

Figure 6b shows the chloride profile measured in the baseline concrete after 60 days exposure. Compared to Figure 6a, Cl accumulation at the interface is considerably less. Table 3 shows peak Cl concentrations measured within 0.5 mm of the steel-concrete interface for the baseline and latex modified concretes. Chloride concentrations in excess of 0.1 w/o were regularly detected for the latex modified concretes, but were not detected for the baseline concrete. The variation in the measured peak Cl level in the latex modified concretes suggests that chloride did not accumulate in a uniform way at the interface. It is likely that cracks allowed rapid transport of brine to the steel surface where it then diffused along the interfacial region. Local regions high in chloride were then created at the base of cracks.

The absence of high interfacial chloride concentrations for the baseline concrete is noteworthy. It is possible that a chloride rich region has not yet been encountered in a baseline concrete sample prepared for EPMA. However, the low interfacial chloride concentrations of the baseline concrete are consistent with EIS data that indicated that large passive interfacial areas were sustained during exposure.

It is possible that latex additions interfere with the concrete's ability to provide corrosion protection for the steel. Latex in the paste may inhibit mobility of cement forming calcium species thereby suppressing self healing of cracks. These open cracks may, in turn, be responsible for the elevated Cl concentrations detected at the steel-concrete interface for the latex modified cements. Reduced mobility of Ca-species at the interface may also inhibit the chemical passivation of the steel since the high pH in the paste may not be maintained over time.

The position of the Cl "front" as a function of exposure time is plotted in Figure 7 as a measure of brine ingress through the paste. Contrary to expectations, brine penetrated further into the latex modified concrete than in the baseline concrete. These data also suggest that the penetration rate for both types of concrete in the first 30 days is much greater subsequent rates.

Summary

Latex modified concrete liners can be prepared using standard centrifugal lining procedures, however it is not clear that latex loading levels can be accurately controlled. Although latex modified concretes have been used successfully in other applications, corrosion test results obtained for these centrifugally cast latex modified concretes do not show a performance improvement over the API standard material. EIS results indicate that the amount of passivated area at the steel concrete interface can be lower when latex is added to the cement mix. EPMA results show that higher Cl concentrations exist at the steel-concrete interface for latex modified concretes. This observation may be traceable to inhibition of crack self healing in the latex bearing concretes. These cracks provide a path for rapid transport of brine to the steel-concrete interface, and may cause locally high

concentrations of Cl in the vicinity of the crack base. Locally high Cl concentrations may result in localization of corrosion damage.

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Table 1. Concrete mixes, final liner thicknesses, and densities for the concretes used in this study.

Material	Cement (kg)	Fly Ash (kg)	Latex Emulsion (kg)	Water (kg)	W/S* Ratio	Final Liner Thickness (mm)	Density (g/cm^3)
Baseline	90.4	60.2	0	54.4	0.36	11.85	2.45±0.07
5% Latex	90.4	60.2	8.8	54.4	0.38	14.50	2.22±0.06
10% Latex	107.8	71.8	22.6	54.4	0.34	12.85	2.24±0.02
15% Latex	98.0	65.3	29.5	41.3	0.31	12.85	2.24±0.02

* Water to Solids Ratio

Table 2. Maximum Corrossion Rates Detected fom Simualted Service Testing.

Liner Material	Corrosion Rate (mpy)
Bare Steel	20*
Baseline	0.0‡
5% Latex	0.6
10% Latex	1.6
15% Latex	0.6

* approximate steady state value

‡ no corrosion detected

Table 3. Peak Cl Concentrations Measured Within 0.5 mm of the Steel-Concrete Interface.

Exposure Time (days)	Baseline	5% Latex	10% Latex	15% Latex
30	0.09		0.01	0.67
60		0.15	0.04	0.03
120	0.08	0.15	0.05	0.20
180	0.08	0.83	0.15	0.04

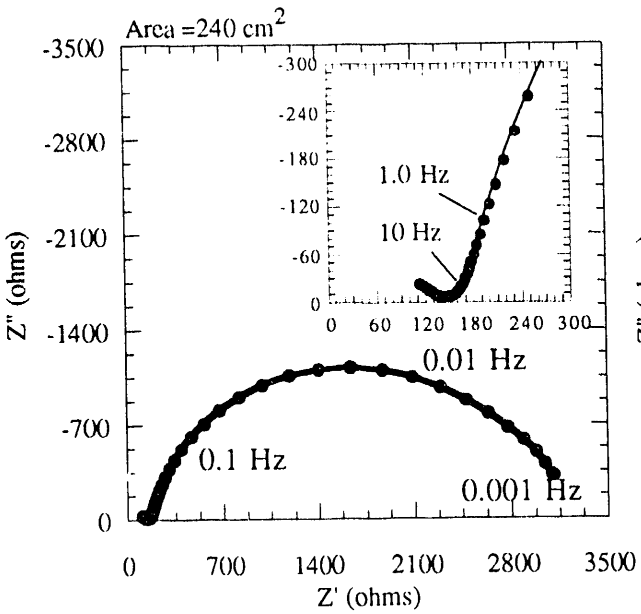

Figure 1. Typical Complex plane plot for the concrete lined steel pipe used in EIS experiments.

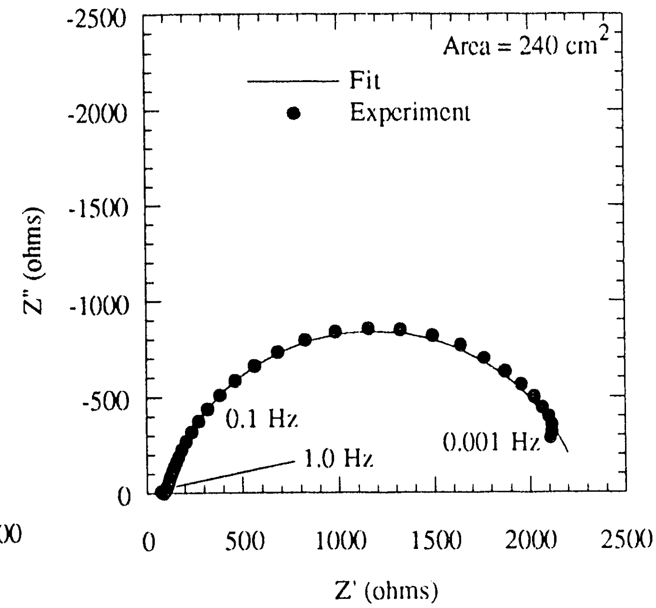

Figure 3a. Experimental EIS data and CNLS fit using the model shown in Figure 2b for the baseline concrete liner.

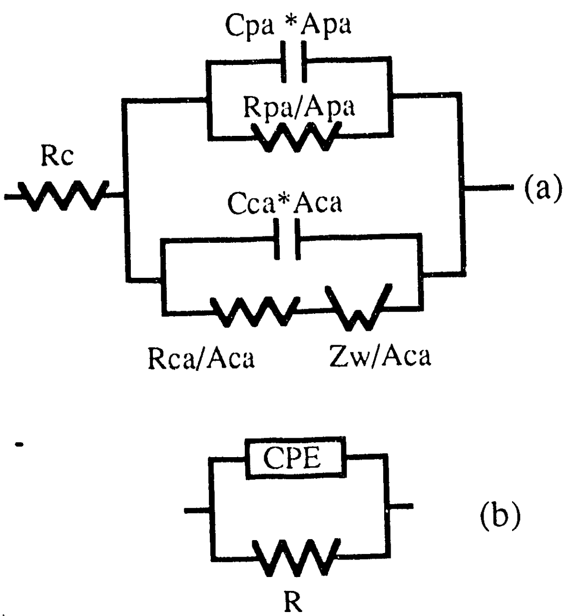

Figure 2. (a.) Equivalent circuit used for interpreting EIS data, (b.) generalized form used for CNLS modeling of the low frequency arc.

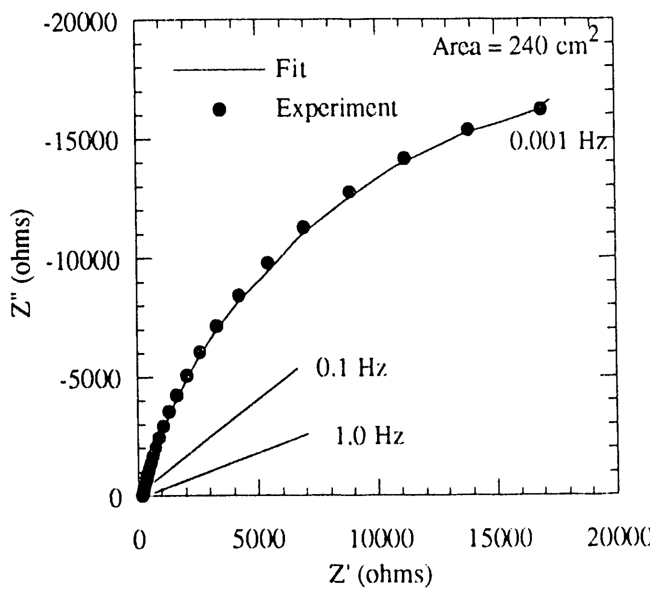

Figure 3b. Experimental EIS data and CNLS fit for 5% latex modifed concrete liner after 14 days exposure.

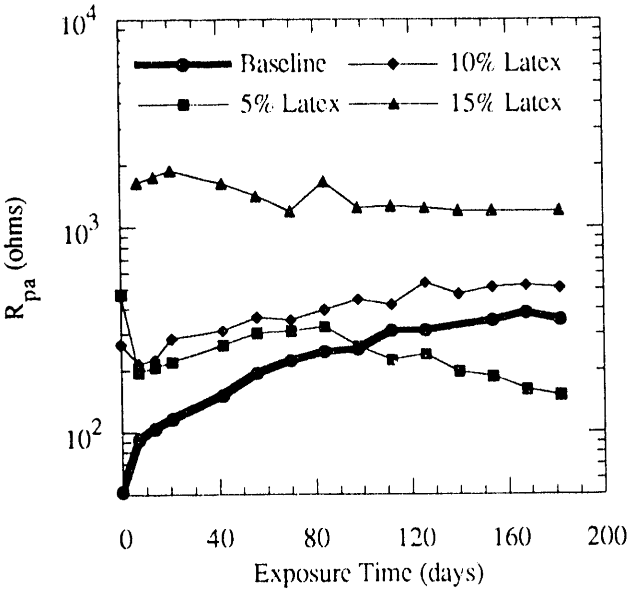

Figure 4. R_{pa}^{m} versus exposure time for the baseline concrete and the latex modified concretes.

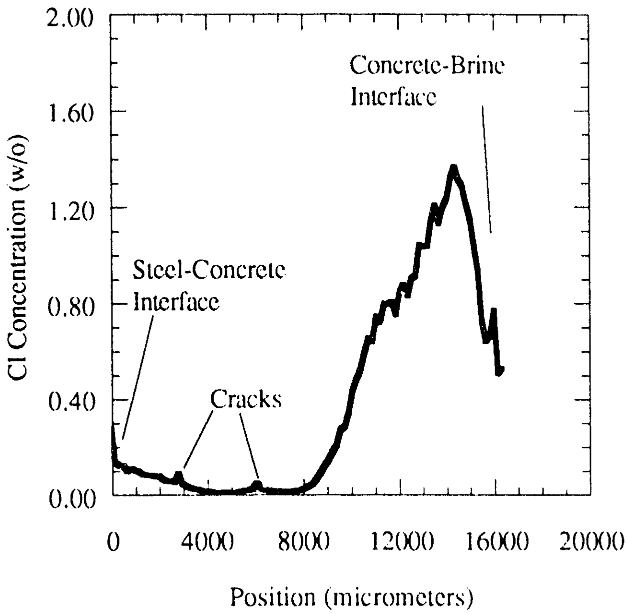

Figure 6a. Cl concentration versus position for the 5% latex modified concrete liner exposed to brine for 60 days.

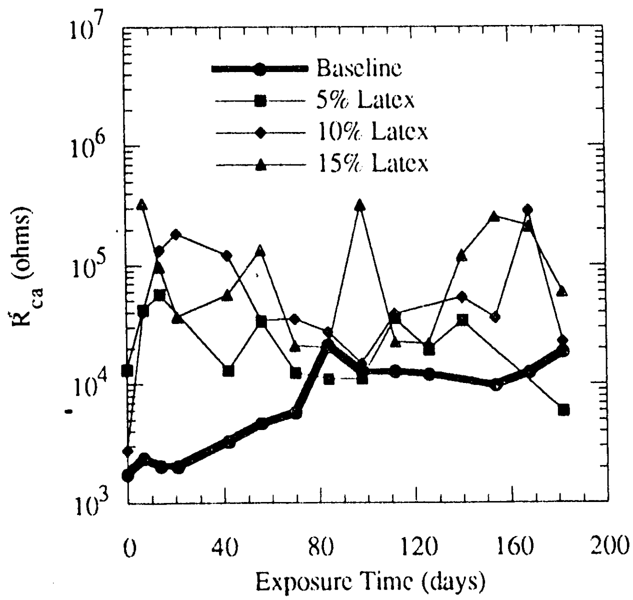

Figure 5. R_{ca}^{m} versus exposure time for the baseline and latex modified concretes.

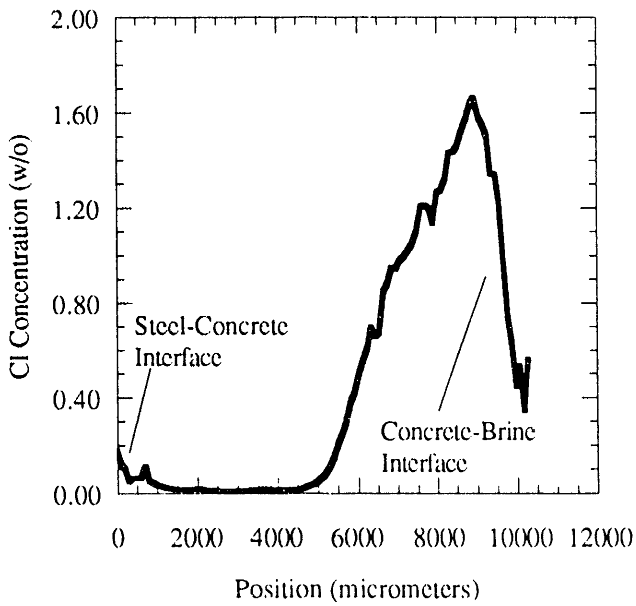

Figure 6b. Cl concentration versus position for the baseline concrete liner exposed to brine for 60 days.

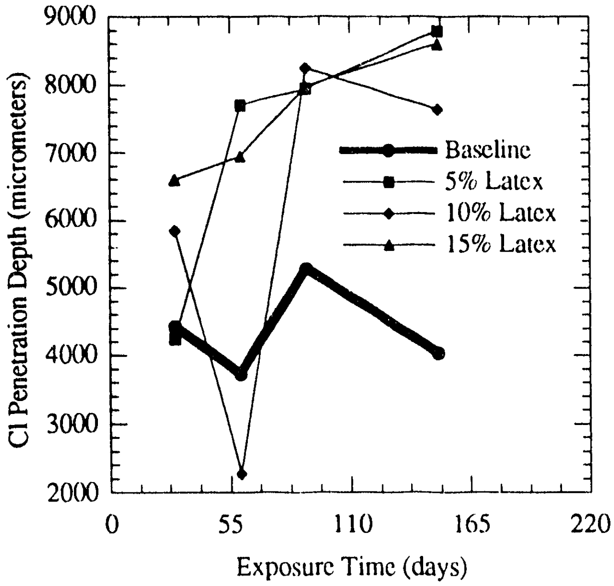

Figure 7. Cl penetration versus exposure time for the baseline and latex modified concretes.

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