Acid Attack on PCCP Mortar Coating

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Abstract

During the failure investigation of a 2.59 meter (102 inch) diameter prestressed concrete cylinder pipe (PCCP) sewer force main, petrographic examination of mortar coating samples revealed that the protective qualities of the coating had been environmentally degraded by exposure to acidic soils. While the mechanisms of carbonation of PCCP from atmospheric carbon dioxide in the form of carbonic acid attack are well documented, relatively little information is available on the effects of acidic soils on PCCP mortar coating. Petrographic examinations of mortar coatings exposed to acidic soil is presented along with discussion of the mechanisms involved in the coating deterioration.

In-situ examination of the failed and adjacent relatively sound pipes showed varying degrees of coating alteration and the resulting loss of thickness. In places the mortar was discolored with a mottled black appearance. Soils at the site consisted of mixed alluvial deposits of sand and blue-grey clay. Since past PCCP failures have resulted from exposure to sodium montmorillonite clay, clay samples were tested for various properties known to be aggressive to PCCP. Of the laboratory results, the reported pH of 5.0 was considered aggressive to PCCP. Petrographic examinations were done on two coating samples from the failed pipe having nominal thicknesses of 8 mm ($^5/_{16}$-in.) and 19 mm ($^3/_4$-in.); and on a 25 mm (1-in.) sample of black discolored coating from the adjacent relatively sound pipe. Severely corroded coating, as thin as 6-mm ($^1/_4$-in.), was present among the samples from the failed pipe. Thickness variation between the samples is too great to be the result of faulty manufacturing process indicating that environmental degradation had indeed occurred in service.

Based on petrographic examinations the effects of acid attack on PCCP mortar coating are: (a) preferential dissolution of the cement paste from the coating surface, which has exposed the siliceous aggregate particles on the coating of the failed pipe; (b) reddish brown stain of iron compounds on the exposed corroded surface; (c) dissolution of calcium hydroxide component of portland cement hydration by the acidic solution; and, as a result (d) a compositional zonation of the paste from the exposed corroded zone through the zones of carbonation (with reddish brown staining from iron compounds), calcium hydroxide leaching, to the sound interior paste. Water absorption and the volume of permeable voids of coatings are higher in the failed pipe than in the sound pipe. The pH of coating from the failed pipe (6.5) is lower than that from the sound pipe (8.0). All these results are consistent with the high degree of corrosion of the failed pipe due to its exposure to highly acidic soil.

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Acid attack on PCCP mortar increases the porosity and permeability of the coating and causes the loss of mass and the loss of strength of coating. The initial reaction involves dissolution of calcium hydroxide (CH) when the strength of coating is minimally affected. Subsequent reactions result in the loss of calcium silicate hydrate (C-S-H) component of cement hydration, formation of hydrated amorphous silica and alumina, and resultant loss of strength. Severity of attack depends on the type and concentration of the acid (the pH of the solution) and the amount and rate of flow of solution through and along the coating surface.

Introduction

The durability of a prestressed concrete cylinder pipe (PCCP) depends upon the resistance of the mortar coating to potentially aggressive chemicals in the exposure environment. Due to the inherent highly alkaline nature of the Portland cement mortar coating in PCCP, exposure to acidic solutions is harmful, causing significant deterioration and loss of the thickness of the coating. Detailed petrographic examination along with determination of the degree of water absorption and the volume of permeable voids in the mortar coating is necessary to determine the quality, density, composition, and degree of impermeability of PCCP to the acidic solutions. Petrographic examination also determines the depth or extent of chemical alteration of the pipe by the acidic solution. Two major concerns of such an acid-induced loss of coating thickness are the significant reduction of the resistance to chloride ingress to prevent corrosion of the prestressing wires and the resulting loss of structural integrity of the mortar. The article described here is a classic case study of severe acid attack on a PCCP that caused more than a 25 percent reduction in the thickness of the mortar coating and subsequent loss of its structural integrity.

Background and Sampling

In Mach 2003 a rupture occurred in a 2.59 meter (102 inch) diameter PCCP sewer force main. Subsequent investigations of the failed pipe revealed significant loss of mortar coating thickness. Field examinations and engineering investigations of the burst and adjacent relatively sound pipes showed varying degrees of alterations and the resulting loss of coating thickness. In places the mortar on the exposed pipes was discolored with a mottled black appearance. As the pipeline parallels a river, the soils at the site are mixed alluvial deposits consisting predominately of sand and blue-grey clay. Knowing that past PCCP failures have resulted from exposure to sodium montmorillonite clay, clay samples were tested for various properties known to be aggressive to PCCP. Of the laboratory results, only the reported pH of 5.0 was considered aggressive to PCCP. Laboratory studies were done on coating samples from the failed pipe having nominal thicknesses of 8 mm ($^{5}/_{16}$-in.) and 19 mm ($^{3}/_{4}$-in.), and on a sample of a black, discolored coating from the adjacent relatively sound pipe having a nominal thickness 25 mm (1-in.). Severely corroded coating down to 6 mm ($^{1}/_{4}$-in.) in thickness was present among the samples from the failed pipe. Specified coating thickness of the 2.59 meter (102 inch) diameter PCCP was 21 mm ($^{13}/_{16}$-in.). While some variability in coating thickness can be expected in manufacture, the extreme thickness variations between the mortar samples was too great to be the result of faulty manufacturing processes and was likely caused by environmental degradation while in service.

Methodology

After detailed visual examinations, scanning, and photographing, the samples were sectioned, lapped, thin-sectioned, pulverized and processed for the following laboratory tests: (a) ASTM C 856, "Petrographic Examination of Hardened Concrete"; (b) ASTM C 642, "Specific Gravity, Absorption, and Voids in Hardened Concrete"; and (c) ASTM C 1152, "Acid-Soluble Chloride in Concrete and Concrete". Additionally, pH testing was done on pulverized samples of both failed and sound pipes from the exposed surface and in the interior to determine the depth of alteration by the acid. Petrography, water absorption, chloride profile, and pH profile are the four common tests necessary to determine the composition, quality, integrity, and depth of extension of acid attack in PCCP.

Petrographic Examinations

Based on detailed petrographic examinations, the mortar coatings are found to be non-air-entrained and made using natural siliceous gravel coarse aggregates; natural siliceous-calcareous sand fine aggregates; portland cements; and water-cement ratios variable in micro-scales in alternating dark and light gray bands of paste and estimated to be 0.42 to 0.44 in the dark gray bands, 0.46 to 0.48 in the light gray bands, and 0.40 or less in the dark, neat pastes of the wire-cast surfaces. The air contents are estimated to be $1\frac{1}{2}$ to $2\frac{1}{2}$ percent; the air contents are higher in the light gray paste than in the alternating dark gray bands.

<u>Aggregates</u> – Coarse aggregates are siliceous gravels having nominal maximum sizes of 13 mm ($\frac{1}{2}$ in.). Particles contain clear to light grey quartz and quartzite and some brown ferruginous sandstone and quartzite. Particles are subrounded to well rounded, dense, massive-textured, uncracked and unaltered. The fine aggregates are natural siliceous-calcareous sands having nominal maximum sizes of 10 mm ($\frac{3}{8}$ in.). Particles contain quartz, feldspar, mafic minerals, limestone and ferruginous rocks. Both coarse and fine aggregates are well graded, well distributed and have been chemically and physically sound during their service in the coatings.

<u>Pastes</u> – Pastes contain alternate light and dark bands – the banded nature is the result of the method of application of the coating and is most prominent in the sound pipe (Figure 1). Pastes are relatively hard and dense in the dark portions and soft and porous in the light areas. Freshly fractured surfaces have semi-conchoidal textures and subvitreous lusters. Residual and relict cement particles are estimated to constitute 16 to 18 percent of the paste volume in the dark colored paste and 10 to 12 percent in the light colored paste. The calcium hydroxide component of cement hydration occurs as small platy and patchy units in the dark and light pastes and is estimated to constitute 8 to 10 percent of the paste volume. Hydration of the cement is normal.

Cross-sections and Surfaces – The exposed surfaces of the coatings are weathered (Figure 2), moderately soft, light to deep reddish brown, carbonated and leached. Loss of coating is severe in the failed pipe, but negligible in the sound pipe. Coating from the failed pipe has a thickness ranging from 8 mm ($^{5}/_{16}$ in.) to a maximum of 19 mm ($^{3}/_{4}$ in.); whereas the sample from the sound pipe has a coating thickness of 25 mm (1 in.) (Figure 1). The inside surfaces are freshly fractured surfaces at the haunch levels of the wires (Figure 2).

Carbonation – The near-surface regions of the samples of both good and failed pipes are carbonated (Figure 3). Carbonation has extended to depths of 3 mm ($^{1}/_{8}$ in.) to 6 mm ($^{1}/_{4}$ in.). In both the sound and failed pipes, however, sporadic carbonation has extended throughout the mortar and particularly concentrated in pastes around the irregularly shaped voids (Figure 4). The neat paste in the wire cast surface is not carbonated (Figure 4), except for a few occurrences of secondary calcium carbonate deposits described below, which may have formed after the removal of samples or in the field.

Air – Air occurs as irregularly shaped voids having nominal sizes up to 3 mm ($^{1}/_{8}$ in.) that are characteristic of entrapped voids (Figures 3 and 4). Entrapped voids are mostly present in the porous areas in light gray bands as gaps between the aggregate particles. The coatings are non-air-entrained and have air contents estimated to be $1^{1}/_{2}$ to $2^{1}/_{2}$ percent. The light gray bands have the higher air contents than the alternating dark bands. The neat pastes in the wire cast surfaces do not have air voids.

Wire Cast Surfaces – The wire cast surfaces have dull textures and are marred by occasional fine, irregularly shaped voids and represent a nominal 1.6 mm ($^{1}/_{16}$ in.) thick layer of neat, hard, firm, dense, dark grey paste having residual and relict cement particles estimated to constitute 18 to 20 percent of the paste volume and a water-cement ratio estimated to be 0.40 or less. The wire casts have center-to-center spacing of 14 mm ($^{9}/_{16}$ in.). Meagerly distributed on the wire cast surfaces are white layers consisting of mixtures of ettringite and calcium carbonate secondary deposits and occasional, isolated, reddish brown corrosion products. The corrosion products are present mostly in the mortar from the failed pipe (Figure 1).

Secondary Deposits – In voids throughout the samples from the 'good' pipe are fine, radiating, acicular crystals of secondary ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$), and lath shaped crystals of secondary calcium hydroxide [$Ca(OH)_2$] (Figure 5). These secondary deposits are indicative of exposure of the coatings to moisture for prolonged periods. Secondary calcium hydroxide deposits in the voids are more abundant in samples from the good pipe but are rare in the samples from the failed pipe.

Evidences of Acid Attack – Paste of the failed pipe shows two distinct evidences of acid attack – one is the significant loss of the thickness of the coating (Figure 2), and the other is the compositional profile of successive layers of outer zones of corrosion, carbonation, leaching and the innermost zone of less altered to sound interior paste (Figure 3). The zone of corrosion is characterized by preferential loss of paste relative to aggregates and as a result proud exposure of the aggregate particles at the surface (Figure 1). The zone of carbonation is characterized by occurrences of very fine grains of calcium carbonate (Figure 3). Immediately underneath the carbonation is a zone of leaching where the paste is devoid of calcium hydroxide that has been leached out by the action of acidic solutions. Due to leaching, the paste is very dark in petrographic microscope and porous (Figure 3). Below the leached zone is the less altered to relatively sound paste where irregularly shaped voids have thin rims of carbonation. Beside these two features, another consequence of acid attack is reddish brown staining at the exposed surface due to the dissolution of ferruginous components from aggregates and paste.

Chemical Analyses

Chloride Analysis – Chloride profile analyses were done using specimens obtained by dry drilling methods. The locations of the samples for chloride profiles are shown in Figure 7. The chloride contents are more or less consistent in two pieces of the good pipe but are variable in two pieces of the failed pipe.

The chloride contents of the neat pastes at the wire cast surfaces of samples from the failed pipe are 0.024 and 0.076 percent by mass of the pastes. The chloride contents in the body of the mortars are from 0.005 - 0.030 percent at the bottom to 0.002 - 0.029 percent at the exposed surface of the coatings. The chloride profiles are indicative of chloride in the mortar-making materials plus an uptake from the environment. Assuming a portland cement content of 20 percent, the chloride values at various depths exceed the maximum 0.06 percent chloride content threshold considered by ACI Committee 222 for minimizing the risk of chloride-induced corrosion of reinforcing steel in non-carbonated, prestressed concrete when oxygen and moisture are present.

pH Test – The respective determined pH of mortar coating samples at the surfaces of the good and failed pipes are 8.0 and 6.5. The pH of the failed mortar pipe is consistent with the reported exposure of the pipe to the acidic soil. All samples show a lower pH at the surface compared to that in the body, which is indicative of their exposure to acidic soil. The higher pH values at the surfaces of the 'good' samples are indicative of a relatively less aggressive environment for those samples. The pH values in the unaltered portions (body) of both sound and failed pipe samples are 12.5 to 13, which are indicative of the inherent high alkalinity of the Portland cement pastes in the bodies of the pipes.

Water Absorption Tests

The average 24-hour absorptions of samples of failed and relatively sound pipes are 6 and 5.6 percent, respectively; the corresponding 5-hour boil-water absorptions are 8.2 and 7.0 percent; and the volumes of permeable voids are 18 and 15.6 percent. Although the failed pipe samples have higher absorptions and higher volumes of permeable voids, which would explain their lesser resistance to the acidic solution than the sound pipe samples, the differences, however, are not significant enough to explain the severe deterioration in the failed pipe but negligible distress in the sound pipe. The soil in the vicinity of the failed pipe must have been highly acidic to cause the observed corrosion of the mortar coating.

Conclusion

Based upon detailed laboratory examinations, the loss of coating and reduction in thickness of the failed pipe are consistent with the reported exposure of the pipe to the acidic soil. The failed pipe has higher water absorption and volumes of permeable voids than the sound pipe. The differences, however, are not sufficient to explain the severe loss of thickness in the failed pipe. There are no noticeable microstructural or compositional differences between these two groups of samples to explain the almost 30 percent variations in their cross-sectional thicknesses.

The higher loss of coating in the failed pipe is due to its exposure to a severe acidic environment indicating that the soil adjacent to the failed pipe has a higher acidity than the soil in the vicinity of the sound pipe. Based on various laboratory studies of concrete and mortar exposed to acidic environment, the severity of the attack is found to be dependent on the type and concentration of the acid and the amount and rate of the flow of solution through the concrete. At a pH between 7 and 8, the calcium hydroxide component of mortar started to dissolve. Calcium silicate hydrate, the main cementitious component of mortar, dissolves at a pH of 7. The attack becomes severe when the pH drops down to 6 and less when the calcium silicate hydrate dissolves significantly and the mortar becomes soft and porous with severe loss of thickness. The determined pH of 5.0 of the clay-rich acidic soil in the vicinity of the failed pipe is consistent with its severe loss of thickness.

Based upon the present case study, PCCP exposed to acidic environment should be dense, well consolidated and made using sound aggregate and a low water-cementitious materials ratio paste. Loss of coating thickness due to acid attack can significantly reduce the protection of prestressing wires from external corrosive agents such as chlorides.

Table 1
Acid-Soluble Chloride Profiles (sample locations are shown in Figure 7)

Location of Section in the Sample	Chloride Content, % by Mass of Sample			
	A1 (Sound Pipe)	A2 (Sound Pipe)	B1 (Failed Pipe)	B2 (Failed Pipe)
a	0.076	0.024	–	–
b+c	0.029	0.006	–	–
d	0.030	0.005	0.019	0.024
e	0.059	0.013	0.027	0.018
f	0.029	0.006	0.004	0.002

Table 2
Absorptions, Specific Gravity and Volume of Permeable Voids

Sample	Absorption (%)		Specific Gravity				Volume of Permeable Voids (%)
	24-hr.	5-hr. Boil	Bulk Dry	After 24-hr. Absorption	After 5-hr. Boil	Apparent	
A1	6.05	8.11	2.183	2.315	2.360	2.653	17.71
A2	5.93	8.47	2.176	2.305	2.360	2.668	18.44
B1	5.58	7.00	2.222	2.346	2.378	2.632	15.56
B2	5.74	7.11	2.218	2.345	2.376	2.634	15.78

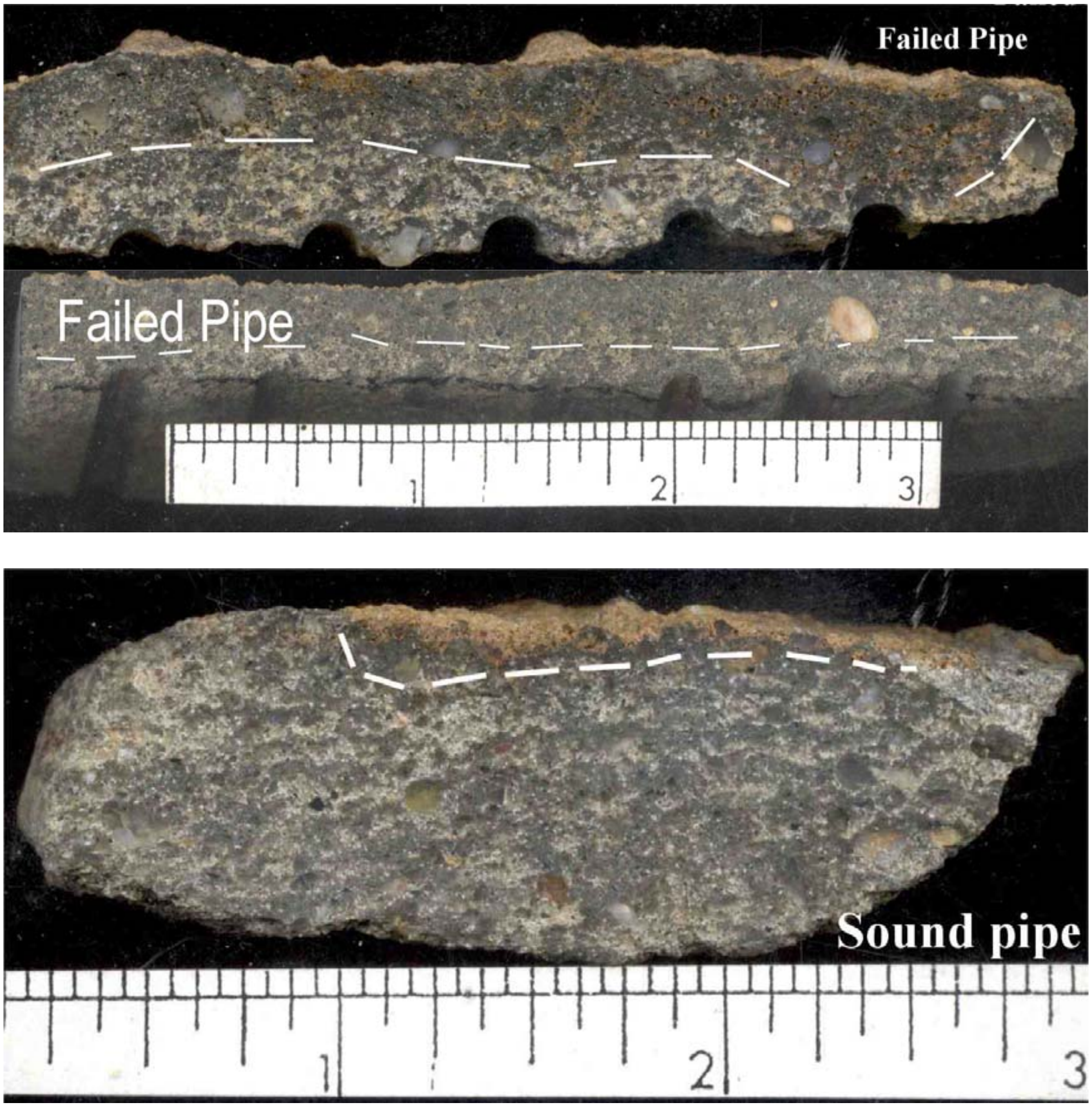

Figure 1. Cross-sections of samples of the failed and sound pipes showing: (a) alternate dark and light colored pastes, (b) reddish brown exposed surfaces, (c) wire-cast surfaces, (d) relatively darker coloration of paste at the top half of the failed pipe sections (above the dashed lines) due to interaction with acidic solutions, (e) distribution and overall good grading of the aggregates, and (f) difference in thicknesses of the failed and sound pipe sections. Scale varies as the photographs have been resized.

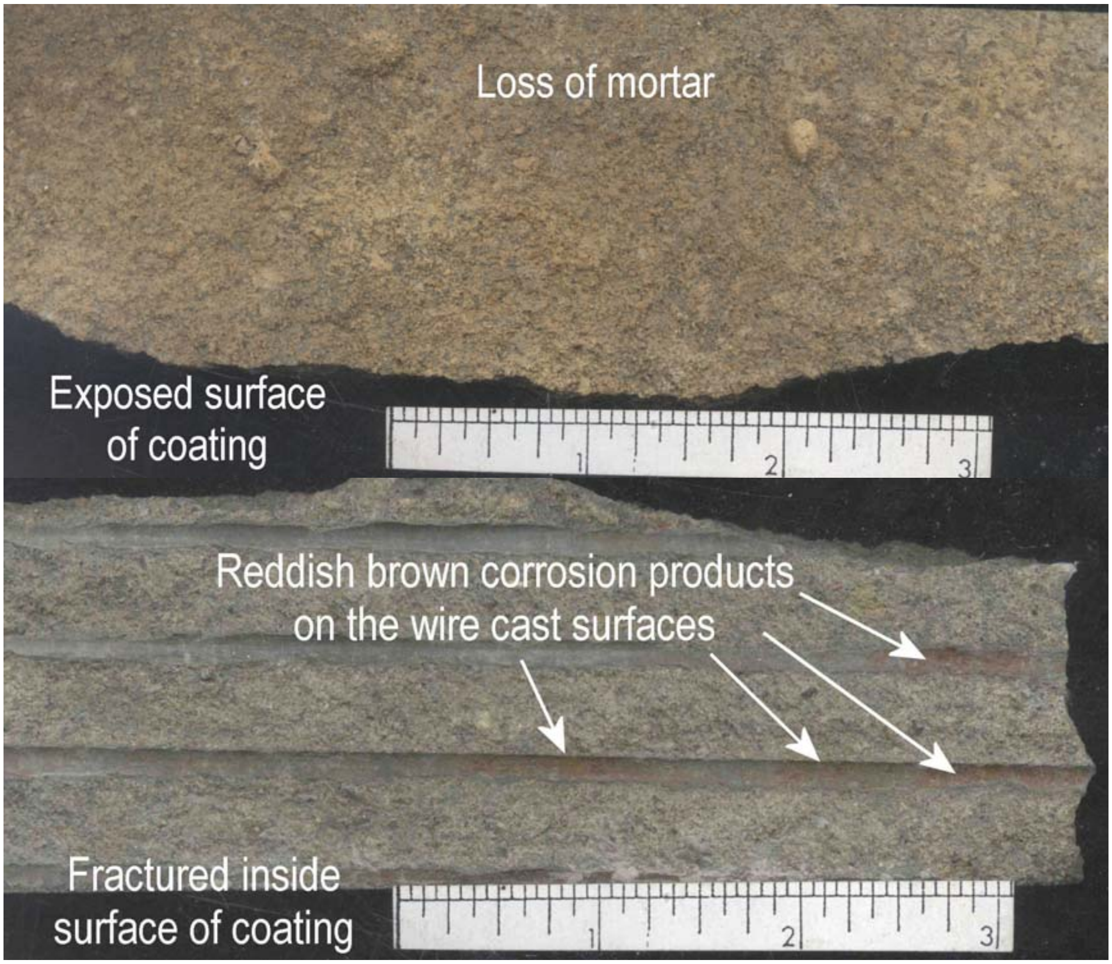

Figure 2. Shown are the exposed surface (top photo) and inside surface (bottom photo) of a mortar sample from a failed pipe. The exposed surface is weathered, reddish brown and has lost a significant amount of mortar due to corrosion in the presence of acidic soil. The fractured inside surface shows parallel arrangements of wire cast surfaces, neat paste on wire cast surfaces and reddish brown corrosion products on the wire-cast surfaces.

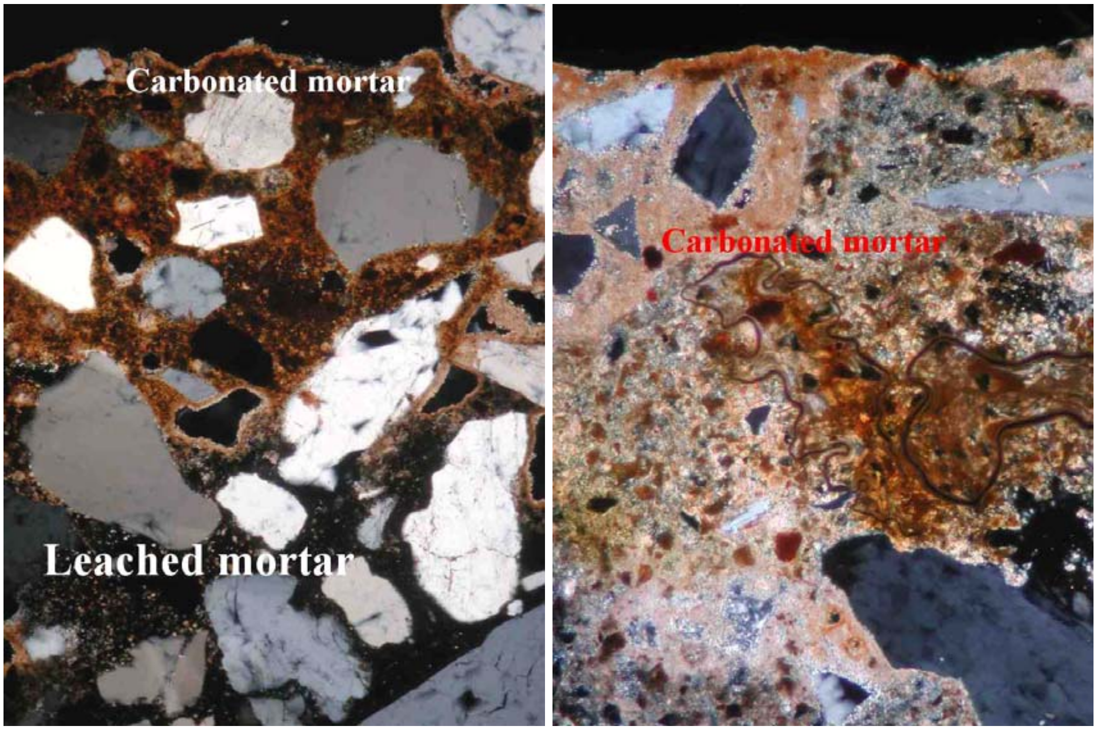

Figure 3. Thin-section photomicrographs showing evidences of acid attack in the microstructure of the mortar coating sample from the failed pipe. The photomicrographs were taken from near the surface region which shows carbonation of coating, reddish brown staining in the carbonated zone (right photo) and a zone of leached paste below the carbonated paste (left photo). Widths of photos = 2.5 mm.

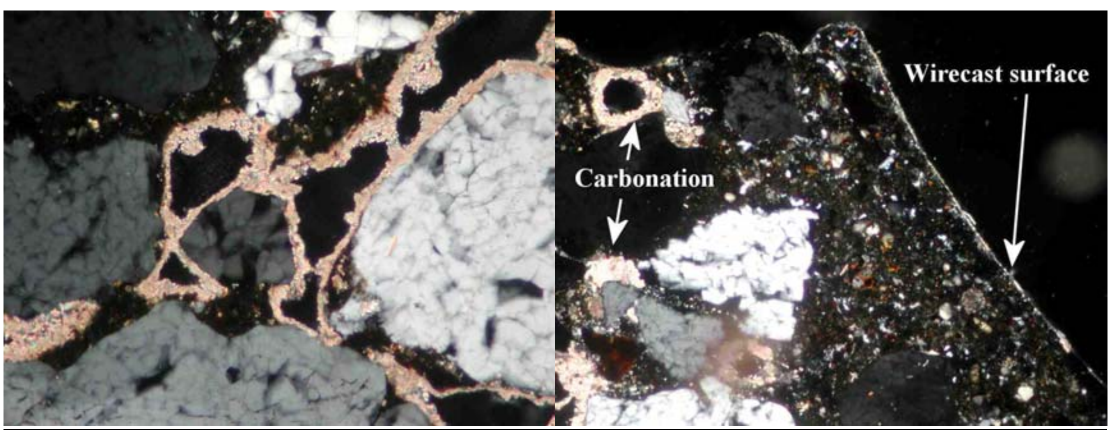

Figure 4. Thin-section photomicrographs of samples of good pipe showing carbonation of paste around the irregularly shaped voids (left photo) but dense, sound, non-carbonated paste at the wire cast surface (right photo). Paste carbonation around irregularly shaped voids is also common in the failed pipe. Widths of fields = 2.5 mm. Widths of photos = 0.15 mm.

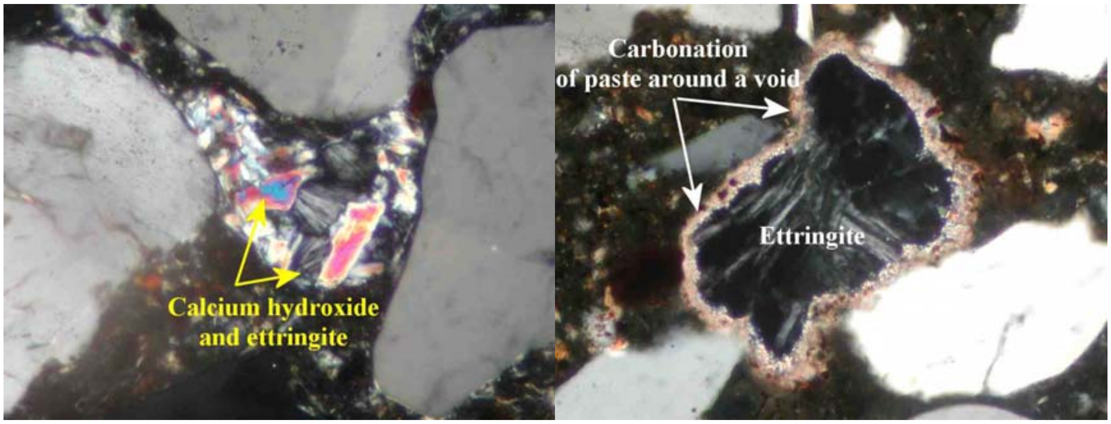

Figure 5. Thin-section photomicrographs showing secondary deposits in the voids and in pore spaces in the paste of mortar coatings – left photo shows large crystals of calcium hydroxide and ettringite and right photo shows ettringite in a void, which has a thin carbonation rim. These features are present in the unaltered portion (body) of both failed and relatively sound pipe. Widths of photos = 0.15 mm.

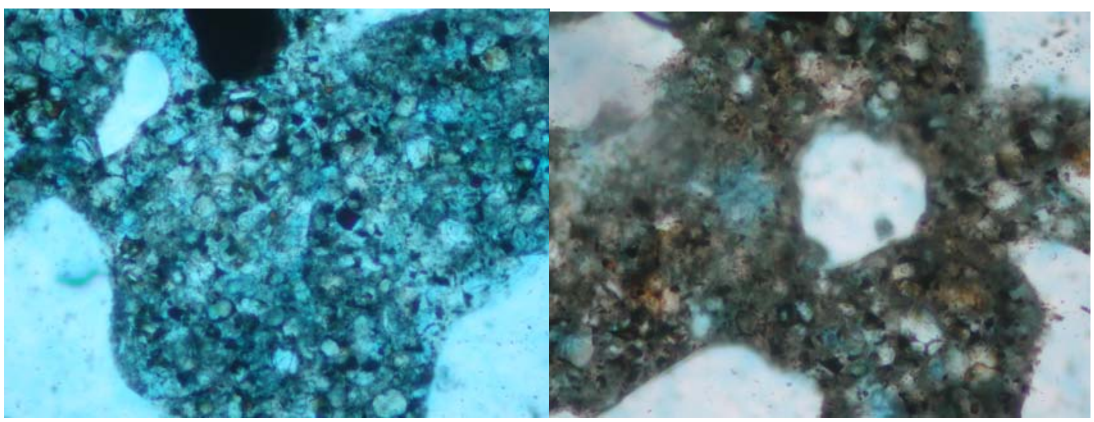

Figure 6. Thin-section photomicrographs showing residual Portland cement particles in the paste in light and dark bands in the relatively unaltered portion (body) of the sound pipe. The left photo is for lighter paste, which is more porous than the denser and darker paste in the right photo. Widths of photos = 0.15 mm.

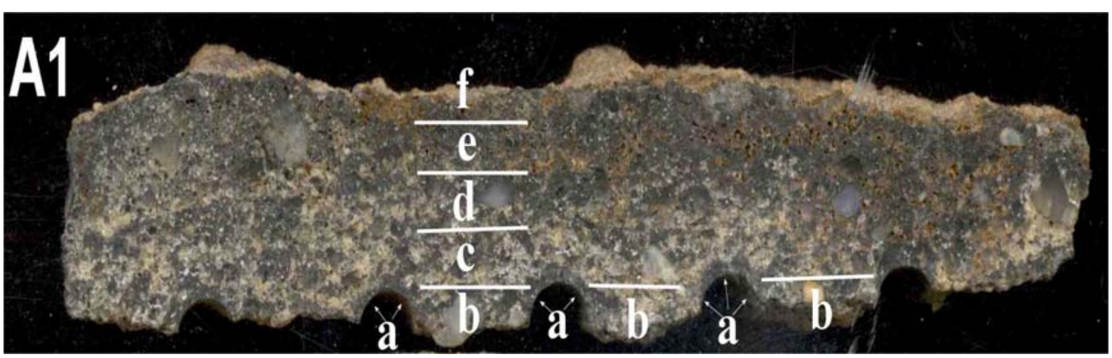

Figure 7. Locations of samples in a cross-section for determining the chloride profile.