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IMPROVED DURABILITY OF IPANEX CONCRETE CONFIRMED BY HOCKING COUNTY, OHIO, FIELD TEST

Background

During construction of bridge deck beams, two concrete test samples were cast on the 6th of February 1991 for the Hocking County, Ohio engineer, both specified as Class "C" concrete with a 3" slump and 4% entrained air. The OHIO DOT specifications for Class "C" concrete are summarized in Table 1.

Table 1. OHIO DOT specifications for class "C" concrete.
Quantities per cubic meter (yard)

Aggregate [size No.57 or No.67]				Cement content [type I]	W/C ratio (max)	Compressive strength [28 day]
Type	Fine	Coarse	Total			
Lime- stone	762	967	1729	356 kg 600 lbs	0.5	28 Mpa 4000 psi
	kg 1285 lbs	kg 1630 lbs	kg 2915 lbs			
Gravel	688	1029	1717	356 kg 600 lbs	0.5	28 Mpa 4000 psi
	kg 1160 lbs	kg 1735 lbs	kg 2895 lbs			

One concrete sample contained no additional admixtures and one contained IPANEX at a dosage rate of 82.8 oz/yd³ (13.8 fluid oz per hundred lbs of cement), the manufacturer's recommended rate. Test samples were taken from the same truck, one before IPANEX was added and one after. They were cast with three reinforcing bars and a hook imbedded into the cylinders parallel to the long axis. The test was devised and implemented by William R. Shaw, P.E., P.S., Hocking County Engineer.

On the 8th of February 1991 after an initial curing time of approximately 48 hours in a heated barn, test cylinders of both specimens were de-molded and immersed into 4 gallons of oil well brine solution to simulate possible local conditions. These specimens remained in open containers of brine at ambient (outside) temperatures for two years and were removed on the 10th of February 1993.

After removal from the brine solution, the samples were allowed to sit in the outside air subject to freeze/thaw cycles for approximately one year, then again immersed in fresh oil well brine from February 1994 to December 1994. The samples were again removed from the brine and stored in air until they were sub-sectioned on the 13th of March 1995. Immediately upon sub-sectioning, they were again immersed in fresh oil well brine until the 28th of July 1999.

Table 2. Time intervals of cylinders' exposure to immersion in brine or outside air.

Brine	Air	Brine	Air	Brine	Air
Feb '91 to Feb '93	Feb '93 to Feb '94	Feb '94 to Dec '94	Dec '94 to Mar '95	Mar '95 to Jul '99	Jul '99 to Aug '99

Observations

1995

The sub-sectioning in 1995 cut off approximately 4" of the bottom of each cylinder. These sub-sections were used only for visual inspection. Figure 1 is a photograph of the two sections. As can be readily seen, the control concrete possesses signs of severe distress.



Figure 1. Control and IPANEX concrete cylinders exposed to oil well brines.

Extensive degradation can be observed on the exposed surface of the cylinder leading to the development of onionskin cracking and spalling. The IPANEX specimen exhibits only minor exterior degradation with traces of weakly developed onionskin separation parallel to the exterior surface.

1999

On the 14th of August 1999, the concrete specimens and samples of the brine, in which they were stored since the 13th of March 1995, were transferred to the Materials Research Laboratory of The Pennsylvania State University for further characterization. Upon receipt, visual observations showed that the control concrete was experiencing extreme distress. The exterior surface of the remaining cylinder was covered with sodium chloride crystals measuring approximately 2 cm in diameter. A pie shaped segment, still containing one section of rebar, had split off from the cylinder revealing extensive corrosion at the matrix/rebar interface and the development of extensive yellow-white growths on the fracture surface of the concrete, Figures 2 and 3

In contrast, the IPANEX concrete remained intact but was covered with fine brown film, most likely a form of iron oxyhydroxide. During the two-and-a-half months that the specimens sat wrapped in plastic exposed to the laboratory environment, several longitudinal cracks developed, however, the integrity of the IPANEX modified cylinder was maintained, Figures 2 and 3.

Results

Due to the severely degraded condition of the control concrete, it was decided that no physical testing could be meaningfully conducted on the specimens. How-

ever, the brine samples that accompanied the concrete specimens and the brine samples in which the specimens were immersed were examined to reveal evidence of the chemical dissolution of the concrete specimens. Table 3 details the bulk chemical analysis of the original brine and brines after exposure to the control cylinder and IPANEX cylinder.

Table 3. Bulk chemical analysis of original brine and brines after exposure to control cylinder and IPANEX cylinder.

[accuracy of analytical data is ±5% of the reported value]

Element	Original Fresh Brine	Brine with Control Cylinder	Brine with IPANEX Cylinder
	Concentration [mg/L]		
Ba	5.1	13.9	7.2
Ca	44,000	79,000	40,000
Fe	280	100	175
K	1,640	2,900	2,050
Mg	7,100	8,300	6,300
Na	52,000	33,000	54,000
Sr	1,330	3,100	1,800
Zn	10.0	45	23.4
Cl	170,000	150,000	170,000
SO ₄	100	808	12.5

This analysis represents all of the major and minor constituents of the brine. An examination of the list also shows that all of the constituents except zinc and chlorine are common to the chemistry of portland cement-based concretes.



Figure 2. Photograph of IPANEX concrete [left] and the control concrete [right].



Figure 3. Photograph of IPANEX concrete [left] and the control concrete [right] rotated 180°.

It would be anticipated that if a concrete specimen degraded in the brine, then the chemical composition of the leachate should reflect the alteration of the concrete. Likewise, if there was little or no alteration, the brine chemistry should not be significantly altered.

Figure 4 graphically represents the data presented in Table 3. From this table and Figure 4 it can clearly be seen that calcium is significantly increased in the brine for the control concrete and that the IPANEX concrete brine and the original unaltered brine have nearly identical concentrations of calcium in solution.

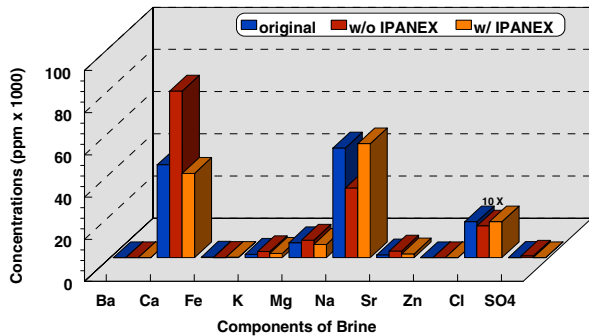


Figure 4. Brine chemistry contrasting the original oil well brine to the brines that were in contact with the concrete for 4-1/2 years.

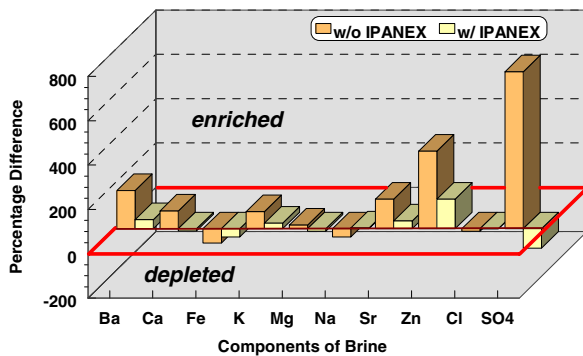


Figure 5. Percentage difference between the solution concentration of elements in the leached concrete samples relative to the original oil well brine.

A careful examination of the data in Figure 5 shows that not only is calcium enriched in the brine from the control concrete but essentially all of the elements except iron, sodium and chlorine also show an enrichment. The depleted elements can be rationalized with respect to their chemical reactions. Iron under these oxidizing conditions will readily precipitate to a ferric oxyhydroxide. The sodium and chlorine depletions can be accounted for in the large mass of sodium chloride salt crystals that decorate the exterior of the control concrete.

In contrast, the IPANEX concrete brine shows only low to modest enrichments associated with the minor and trace elements in portland cement, for example, barium, strontium and zinc. The principal cement-containing elements common to the brines are nearly at the original brine concentrations.

Conclusions

The visual analysis of the two concrete specimens, that were designed and cast in Hocking County, Ohio, and met OHIO DOT specifications, clearly demonstrated that *unprotected* concrete rapidly degrades in the presence of oil field brines, Figure 6. This observation was further supported by the analysis of brine used as a leachate for the samples. Significant enrichments in concentration of the elemental constituents of the concrete are observed dissolved in the brine which contained the control concrete.



Figure 6. Photograph of the control concrete after alternate exposure to 7 years 3 months in brine and 1 year 3 months in air.

Durability of concrete is impacted by the mass transport of agents in water into the interior of the concrete via the interconnected network of pores that constitute the total porosity of the concrete. Deleterious

agents such as sulfate ions, chloride ions, oxygen and carbon dioxide comprise the suite of chemicals that are routinely identified as being responsible for degradation. In the example studied in this paper, chloride ion ingress into the control concrete resulted in a rapid alteration of the concrete, which was manifested by an uptake into the leachate of elemental constituents of the concrete. More specifically, calcium ions dissolved out of the control concrete resulting in the degradation of the C-S-H. The condition of the IPANEX cylinder and the lack of degradation, as manifested in the leachate chemistry, strongly supports the position that the ingress of chloride ions into the IPANEX concrete was significantly retarded over the life-time of this eight-and-a-half-year study.

IPANEX concrete, Figure 7, exhibits only minor alteration and minor release of elements from the concrete into the brine leachate after approximately eight-and-a-half years of alternate exposure to immersion in this corrosive oil well brine and freeze/thaw conditions in air.



Figure 7. Photograph of IPANEX concrete after alternate exposure to 7 years 3 months in brine and 1 year 3 months in air.

The service life of a concrete structure is predominately controlled by the microstructural quality of the concrete matrix.

Environmental Scanning Electron Microscopy (ESEM) shows that IPANEX concrete enjoys a more continuous microstructure than control concrete. Borders of hydrating cement grains in IPANEX concrete extend beyond those of control concrete and grow into a more continuous matrix of hydrated paste.

IPANEX contains calcium silicate hydrate (C-S-H) which improves hydration by a nucleating (seeding) action resulting in an intensification of, or more wide spread, crystallization of C-S-H. C-S-H particles are dispersed on a microscopic level initiating precipitation of and intensifying hydration of cement particles, resulting in improved hydration conditions and a more refined microstructure.