Sulfate Limits for Corrosion of Steel Strand in Deficient Grout

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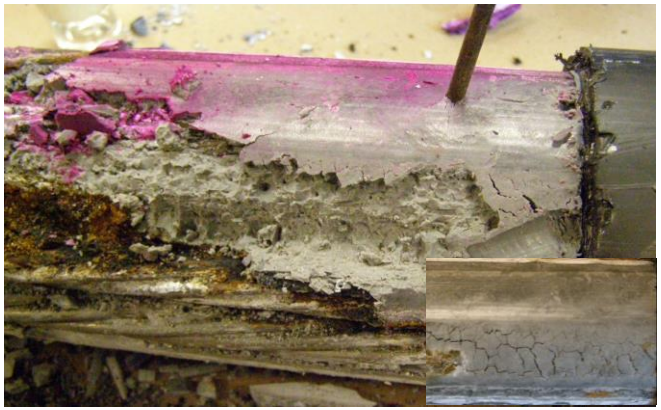
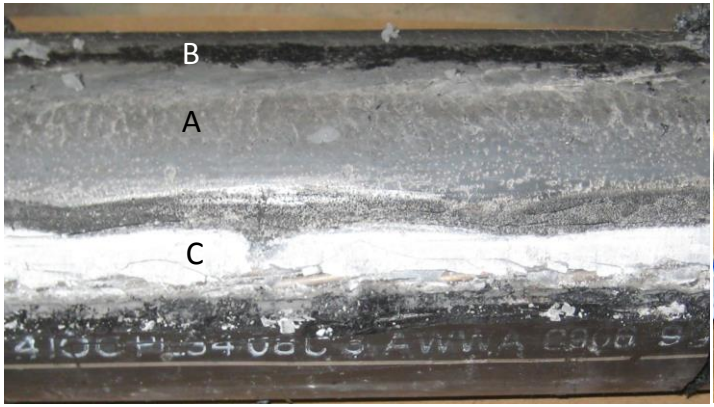
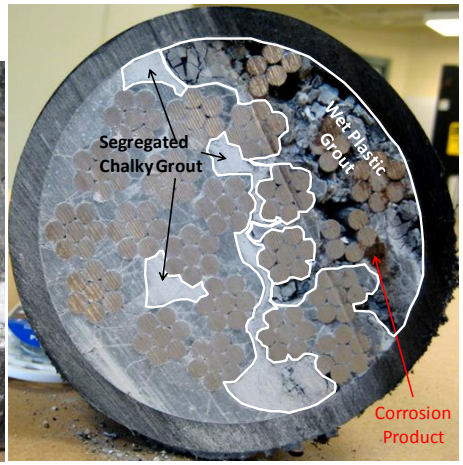
Introduction

- Severe corrosion of PT- tendons in Florida bridges utilizing pre-packaged thixotropic grout products.
- Deficient grout was characterized as having poor cohesive bulk properties, high **moisture content**, high **pH** and **enhanced sulfate ion** concentrations.
- The severe corrosion was well associated with the deficient grout and not necessarily with the presence of bleed water, voids, carbonation and chlorides
- In separate cases, quality control issues with chloride contamination and other factors
- Limited information was available on the corrosion behavior of PT strand in grout materials with enhanced sulfate content.







Existing Sulfate Limits

Standard	Sulfate Limit		Classification
ACI 318	150 < SO_4 <1500 ppm	Moderate	Water
	1500 < SO_4 <10,000 ppm	Severe	Water
	SO_4 > 10,000 ppm	Very Severe	Water
BS EN 196	SO_4 < 2000 ppm		Concrete Mix Water
EN 206	200 <SO_4< 600 ppm	Slightly Aggressive	Water
	600 <SO_4< 3000 ppm	Moderately Aggressive	
	3000 < SO_4< 6000 ppm	Highly Aggressive	
CCAA*	SO_4 < 400 ppm	GP,GB Max W/C = 0.55	Water
	400 < SO_4 < 6000 ppm	SR Max W/C = 0.45 – 0.55	
USBR	< 150 ppm	Negligible	Water
	150 to 1000 ppm	Positive[1] (mild)	
	1000 to 2000 ppm	Considerable[2](moderate)	
	>2000 ppm	Severe(high)	

* Based on recommendations from Cement Concrete and Aggregate Australia
[1]Type II cement , [2]Type V cement

- Many agencies provide sulfate limits for concrete material durability.

Problem Statement

- Steel corrosion occur in deficient grout with enhanced sulfate ion concentrations
- Corrosion research addressing chloride contamination did not consider the presence of deficient grout (possibly enhanced sulfate ion)
- Existing test methodologies do not address grout robustness and corrosion durability

The work was aimed to identify possible practical limits for sulfates in corrosion initiation of steel in grout

Test Methods

Studied parameters : corrosion potential (OCP), current density, grout chemical analysis and visual inspection

Electrochemical Tests in Sulfate Solutions

- Sulfate solution (pH=13.3 and 12.6)
- Premixed and incremental sulfate solutions
- Naturally aerated conditions
- Preconditioned 1 day in solution at OCP or -1V_{SCE}
- Anodic polarization (-1V_{SCE} to +500mV_{SCE}) at 0.05mV/s.

Test Method To Assess Corrosion Behavior and Grout Robustness

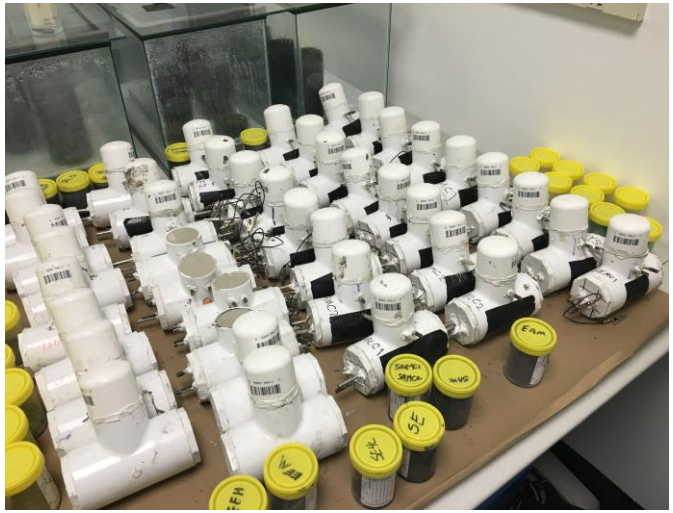
Modified Inclined Tube Test (MIT)

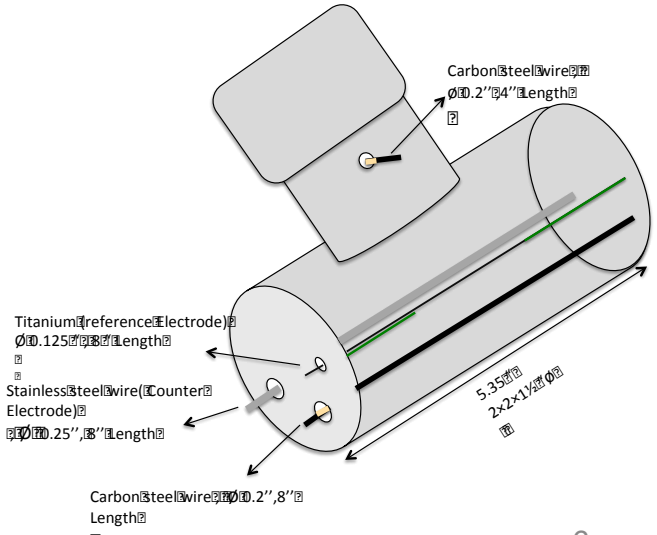
- 15 feet tendon mockup cast
- 0 %, ~0.09%,~0.9%,~5.5% sulfates by cement weight.
- 0.08% , 0.2 % chlorides by cement weight.
- Expired grout, excess mix water
- Corrosion probes - plain and crevice
- Cast at 30° inclination.

Test Method To Assess Corrosion Behavior and Grout Robustness

Inverted Tee Test– (INT)

- Cast in (2×2×1½” ø, 4 ¾” length) PVC tees
- Tee was expected to facilitate volume displacement of deficient grout to the top
- Raw grout product were kept in 100% relative humidity for one month
- 20% excess water than recommended
- Control case mix as recommended





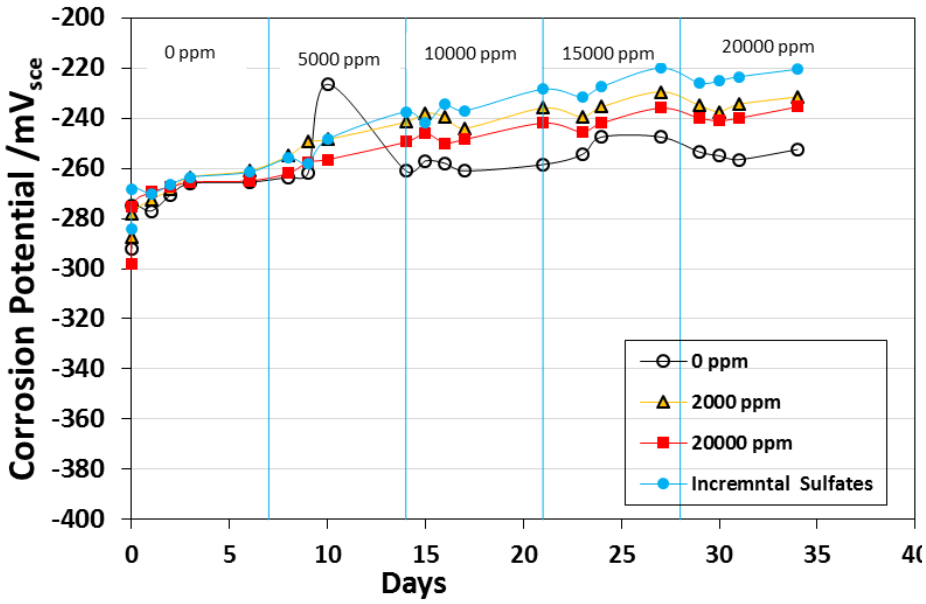
Test Conditions

- Grout product – A & B
- 0 ppm, 2000 ppm, 20000 ppm and 100,000 ppm sodium sulfates
- 0, 0.08 %, 0.2 % by cement weight of chlorides

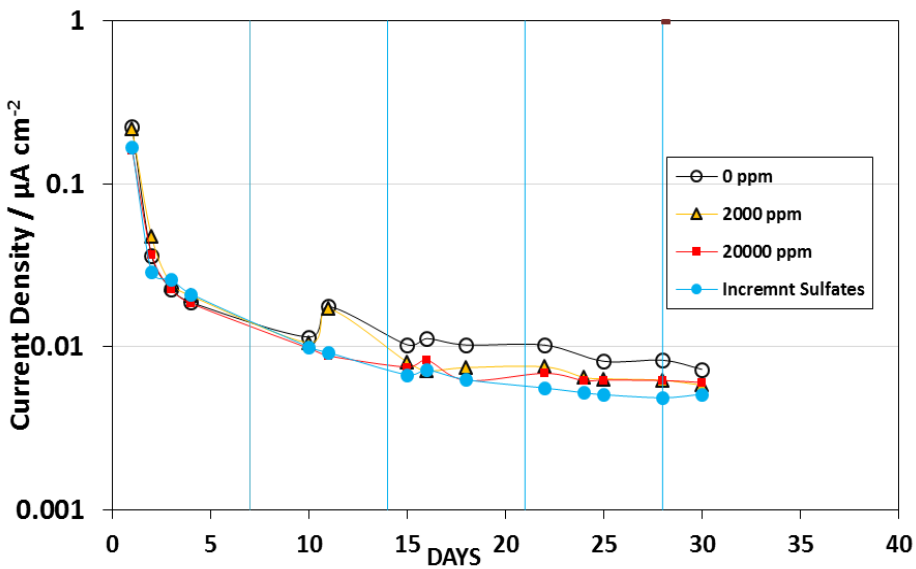
13.3 pH

Electrochemical Tests in Sulfate Solutions

Corrosion Potential



Current Density

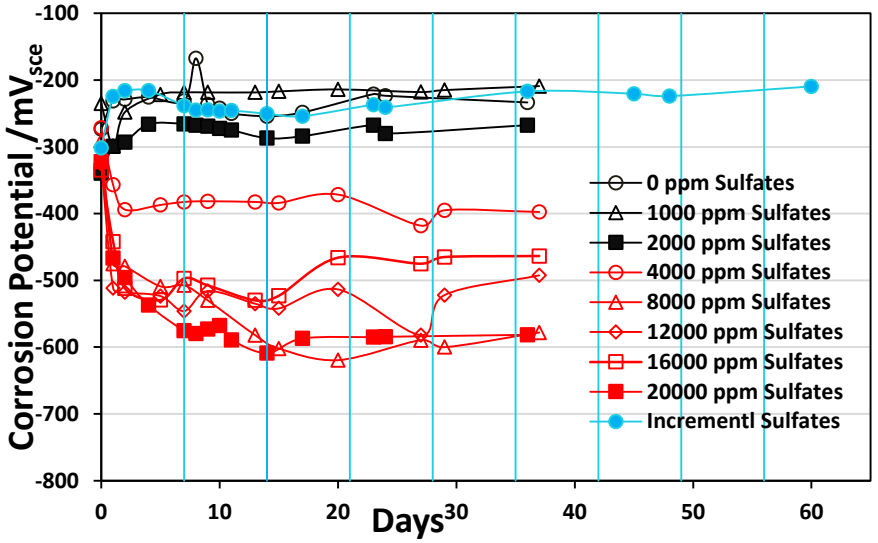


- Passive like potentials in all test conditions in 13.3 pH.
- The corrosion current density was low (approx. < 0.01 mA/cm^2)
- Levels of sulfates showed mild effect on increasing the potentials more noble than in control case.
- No corrosion activity measured for samples with incrementally added sulfates as high as 20,000 ppm sodium sulfates

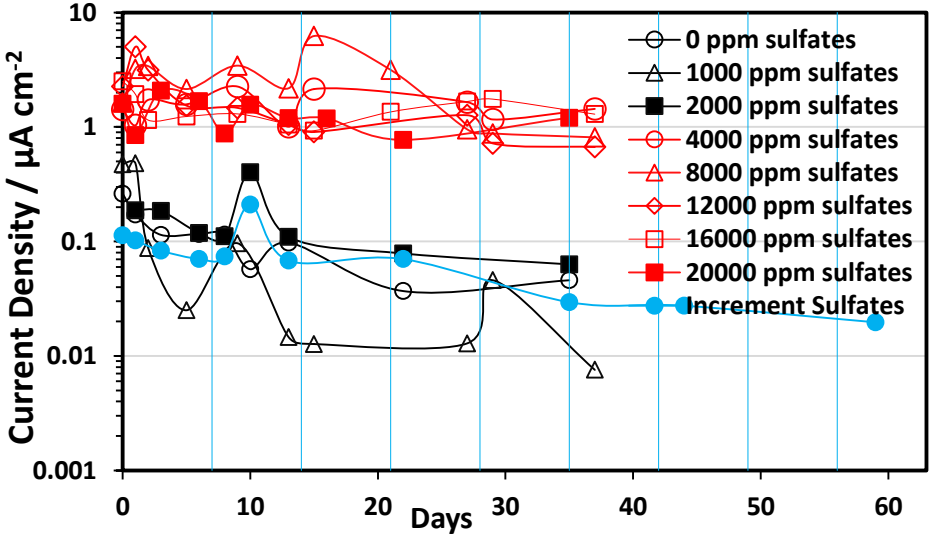
12.6 pH

Electrochemical Tests in Sulfate Solutions

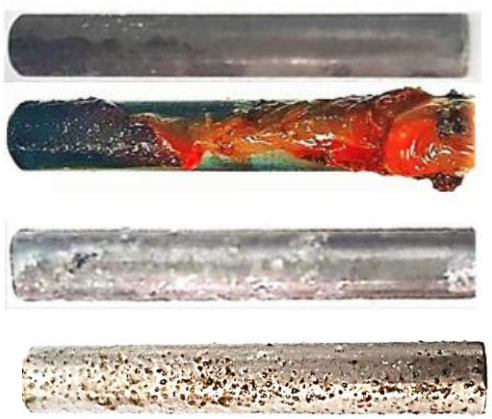
Corrosion Potential



Current Density



- Steel samples in greater than 4000 ppm pre-mixed sodium sulfate solutions showed enhanced corrosion activity.
- However corrosion activity less for samples with incrementally added sulfates as high as 65,000 ppm sodium sulfates up to 60 days
- Polarization tests showed effect of sulfates on steel corrosion modality (passive film development)



Day 35, 2,000ppm Na_2SO_4

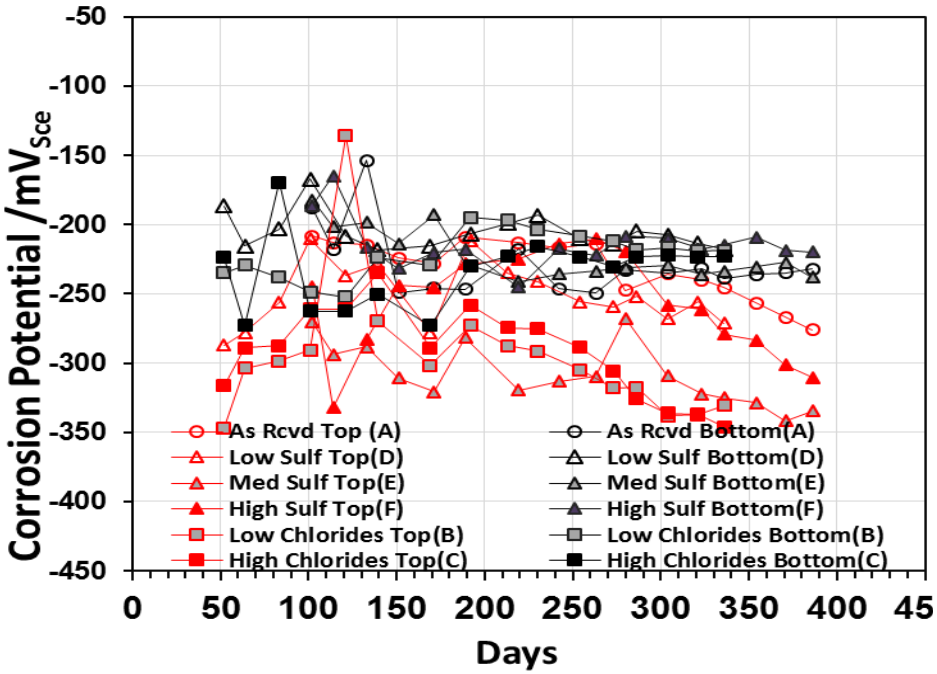
Day 35, 20,000ppm Na_2SO_4

Day 63, (Incremental sulfate addition) 65,000ppm Na_2SO_4

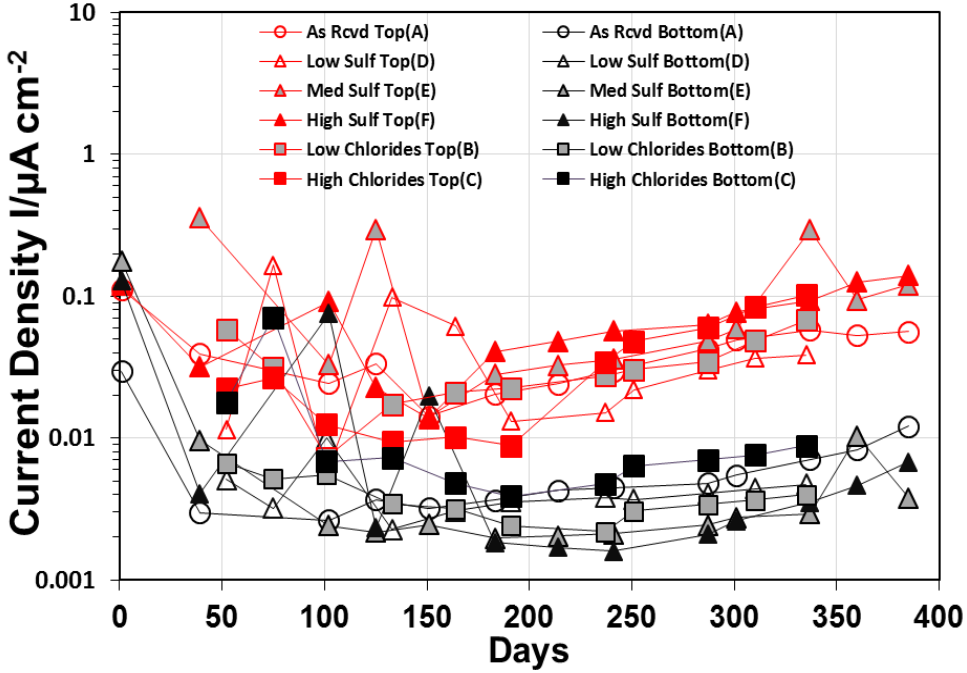
Polarized samples (20000 ppm Na_2SO_4)

Corrosion Behavior in Modified Inclined Tube Test (MIT)

Corrosion Potential

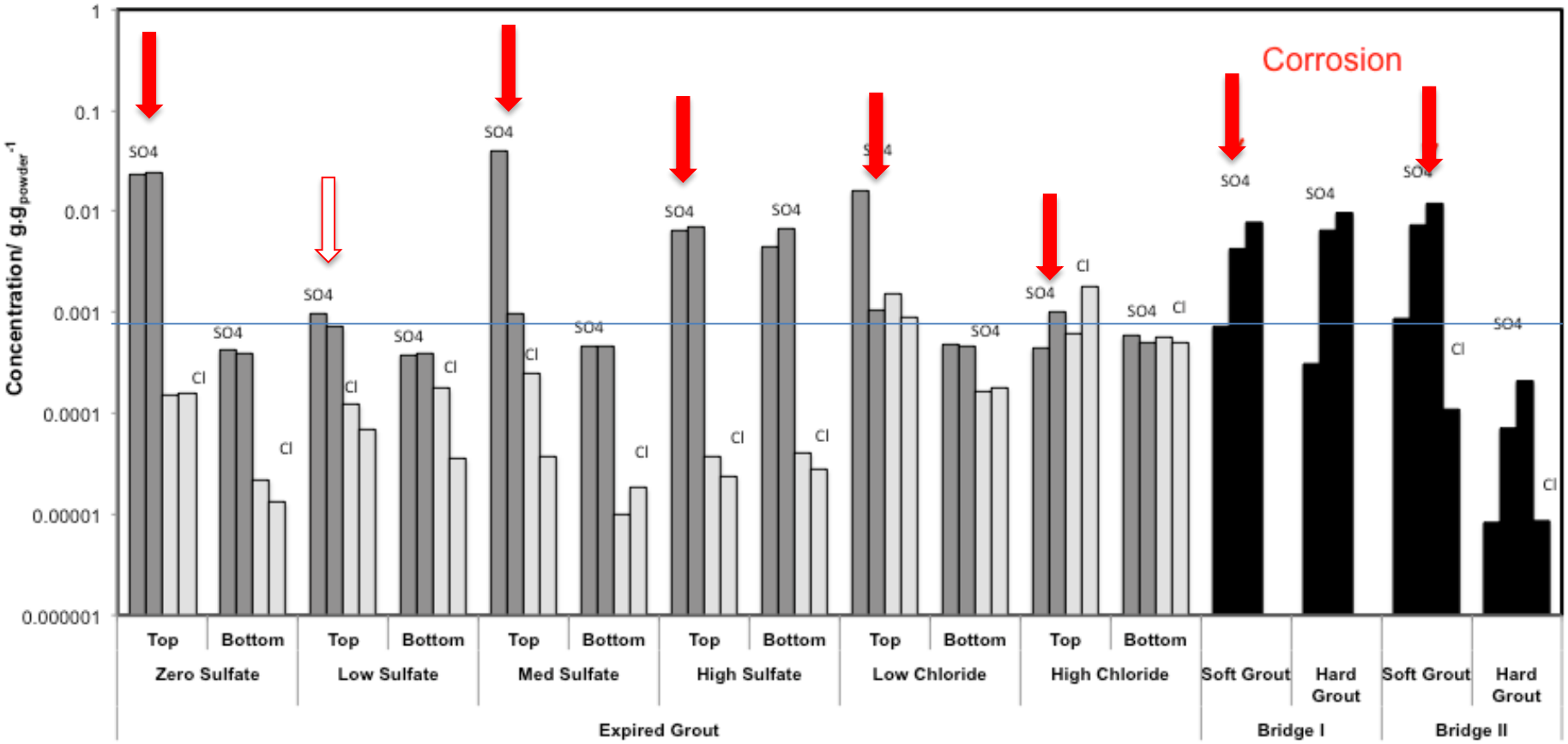


Current Density



- Corrosion potentials (~< -300mV$_{SCE}$) and current density (~ 0.1 mA/cm^2) indicative of greater corrosion activity in top portion of all tendon including zero admixed sulfate condition.
- Greater corrosion activity for steel at the top portion of tendon where deficient grout is found.

Sulfate Content in Modified Inclined Tube



- The test results indicate the top part of the tendons tend to have higher levels of sulfate concentrations.
- In comparison to the resolved sulfate content measured in grout from Bridge I and II, it is seen that separation of grout material can allow for accumulation of sulfate ions without external sulfate sources.

Corrosion in Modified Inclined Tube Test (MIT)

TOP

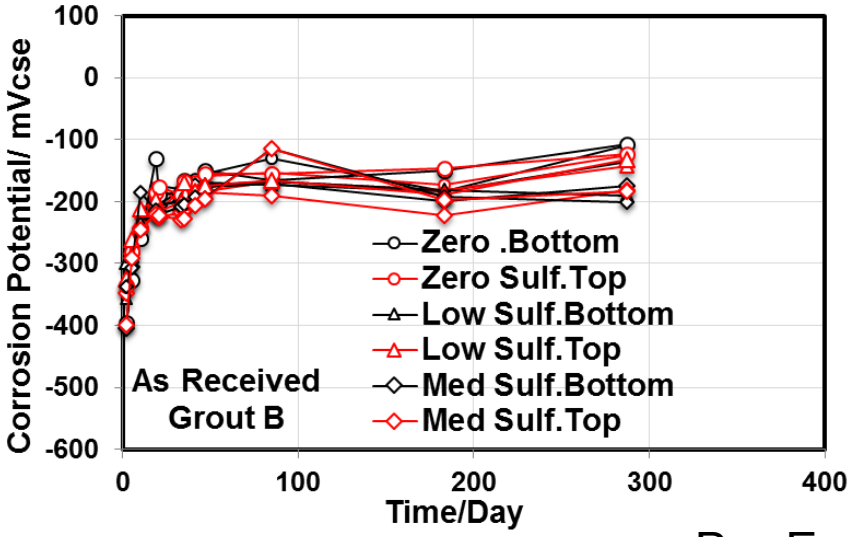
BOTTOM

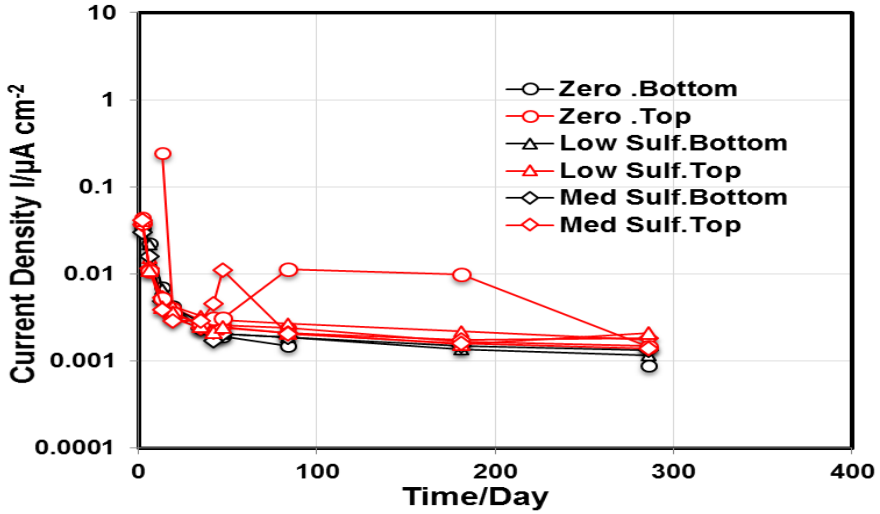
- Steel corrosion only observed in deficient grout.
- Deficient grout localized only at high elevations.
- pH of grout ranged from 11 to 13 (pH indicator)
- Corrosion of steel in deficient grout with ~ 0.0004 to 0.04 $g_{sulfate}/g_{powder}$ (typ >0.0007g/g)
- Similar values to steel corrosion in deficient grout in bridges ~ 0.0007 to 0.012 $g_{sulfate}/g_{powder}$

Corrosion Behavior in Inverted Tee Test (INT)

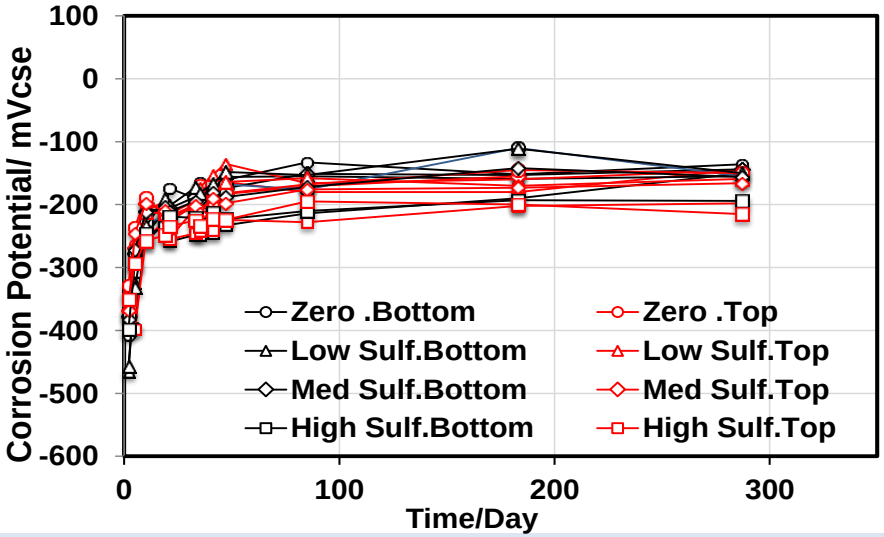
Grout B

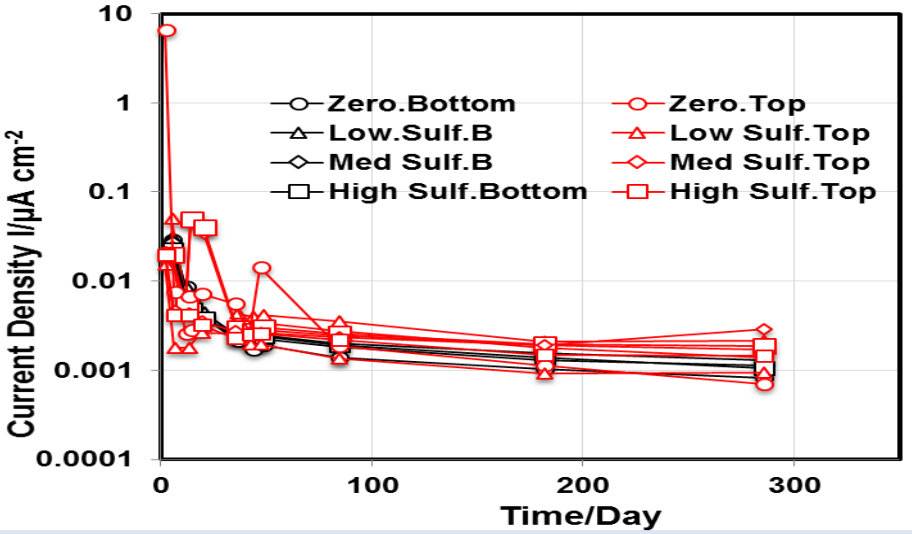
As Received Conditions





Pre-Exposed Conditions



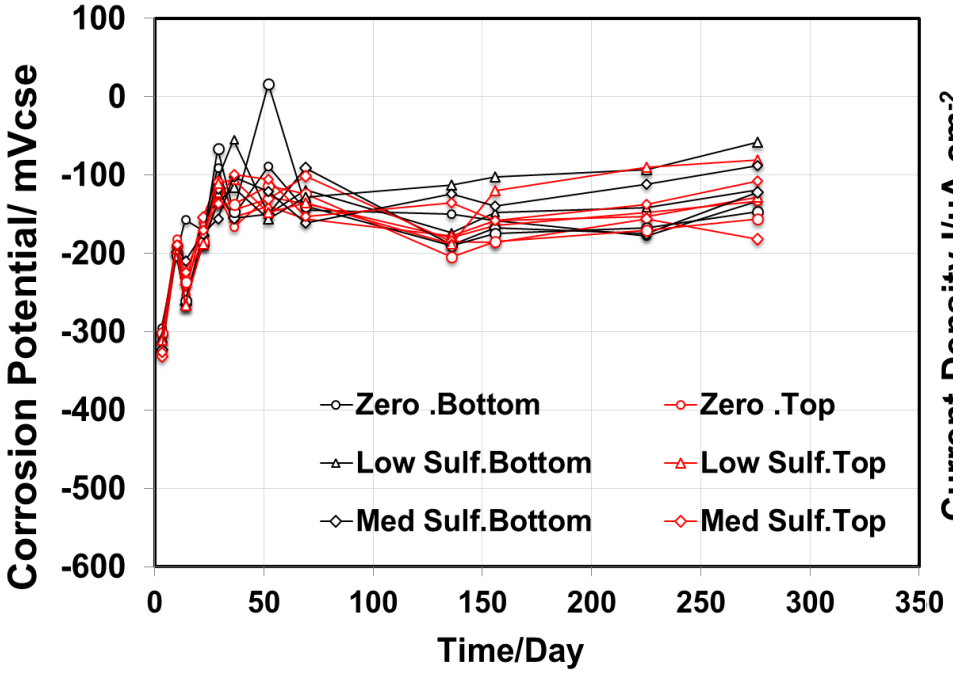


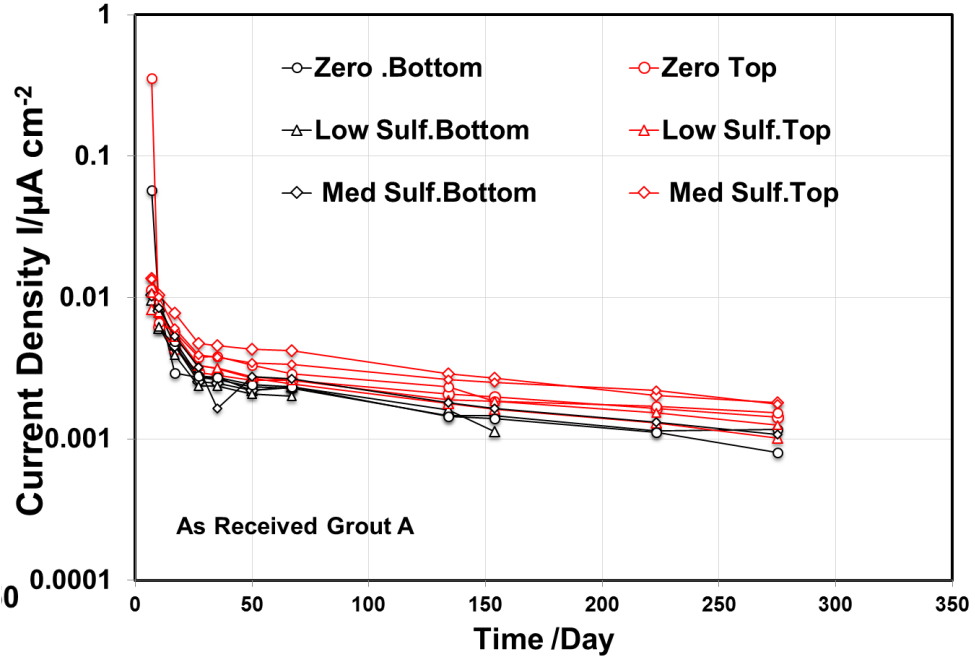
- Steel samples in Grout B did not exhibit active corrosion behavior in all test conditions.

(Low Sulf: 2,000ppm /Med Sulf: 20,000ppm/High Sulf: 100,000 ppm)

Corrosion Behavior in Inverted Tee Test (INT)

Grout A (As Received)





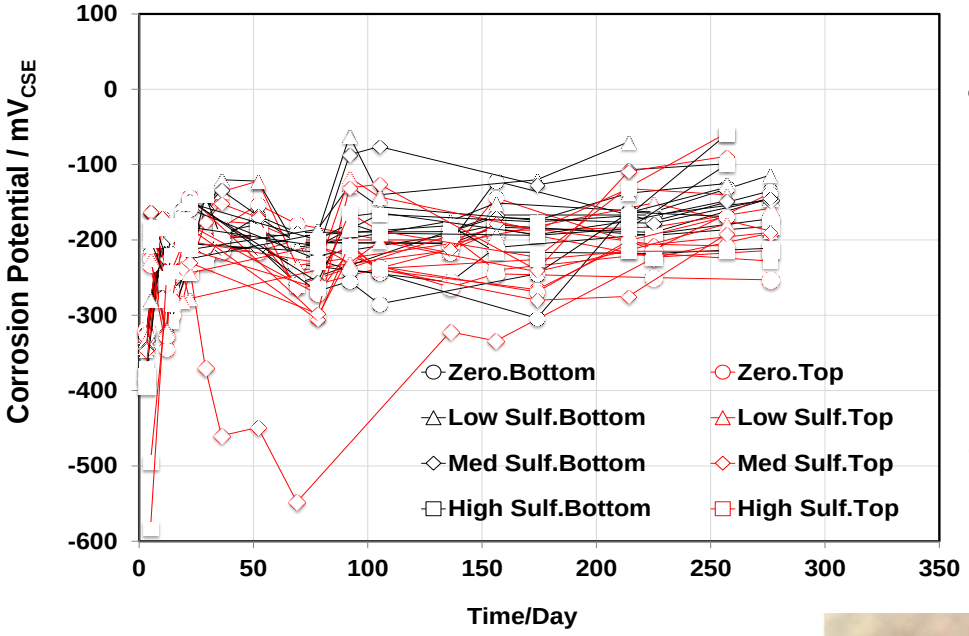
- Steel samples in Grout A did not exhibit active corrosion behavior in as-rec'd test conditions.
- Sulfate level in tee header < 0.00052 $g_{sulfate}/g_{powder}$

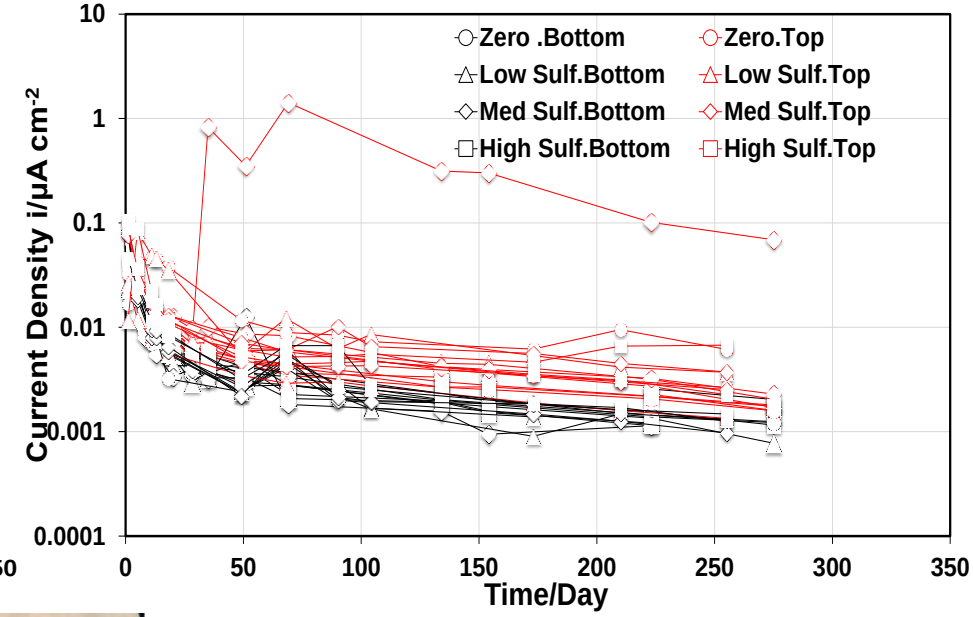
(Low Sulf: 2,000ppm /Med Sulf: 20,000ppm/High Sulf: 100,000 ppm)

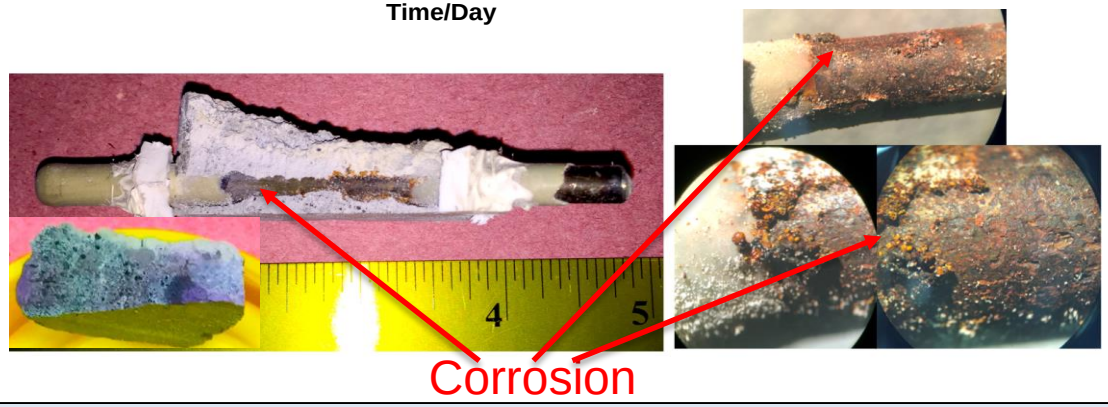
Corrosion Behavior in Inverted Tee Test (INT)

Grout A (Pre-Exposed)

Admixed Sulfates







- Corrosion of steel in deficient grout observed (i > 0.1 uA/cm^2)
- Deficient grout in tee header
- Corrosion of steel in tee header with > 0.0164 $g_{sulfate}$ / g_{powder}

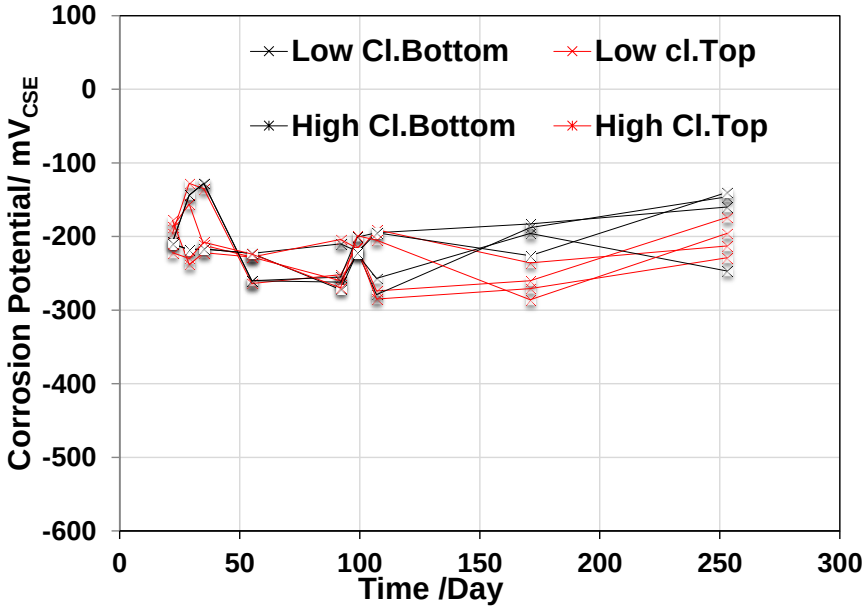
❑ INT and MIT test methods can promote grout segregation and differentiate grout robustness to adverse mix conditions and identify corrosion activity

Corrosion Behavior in Inverted Tee Test (INT)

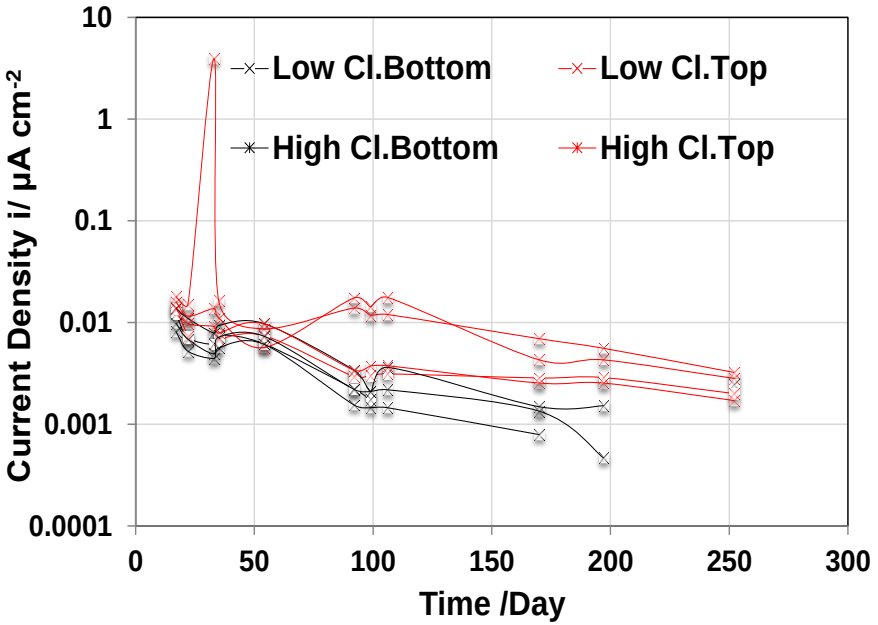
Grout A (Pre-Exposed)

Admixed Chloride

Corrosion Potential



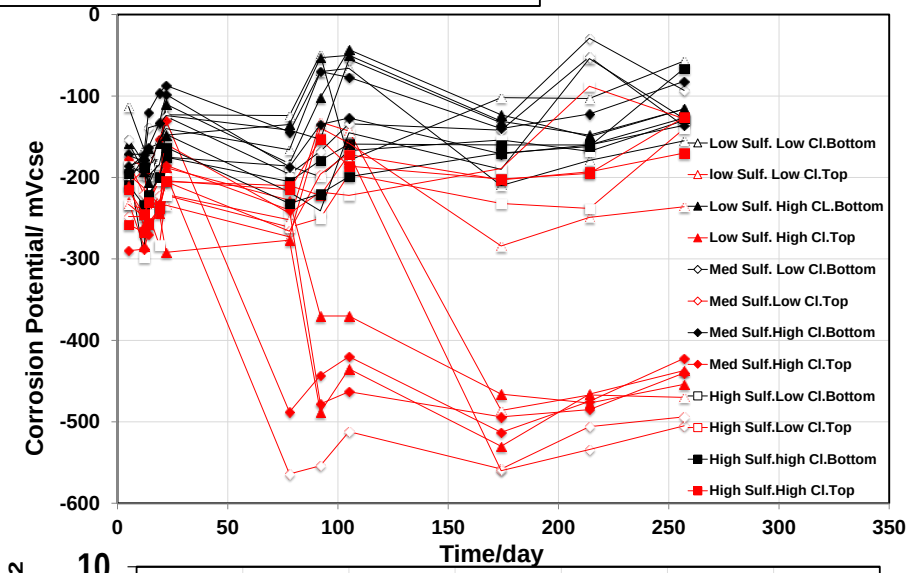
Current Density

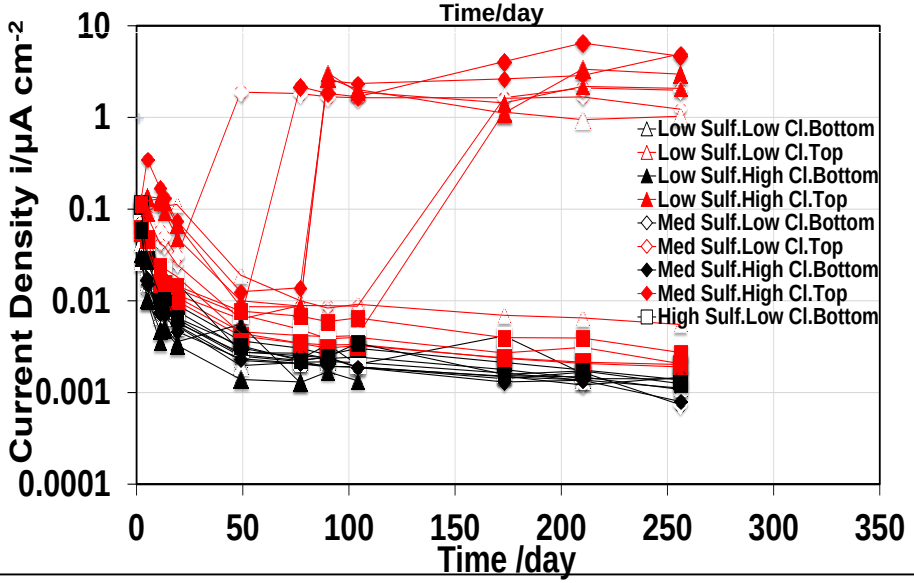


- No indication of corrosion development in presence of admixed chlorides up to 0.2%.
- The physical consistency of the grout in the tee header for these samples was not the wet and highly friable material characteristic of corrosive deficient grout observed elsewhere

Corrosion Behavior in Inverted Tee Test (INT)

Grout A (Pre-Exposed)

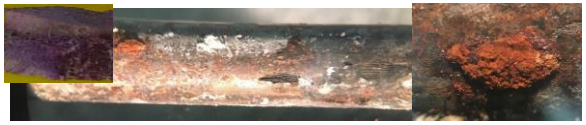




Testing of chloride content in raw material alone where grout may be susceptible to segregation is insufficient to determine corrosion risk

Combined Admixed Sulfate and Chloride

Low Sulfate, Low Chloride



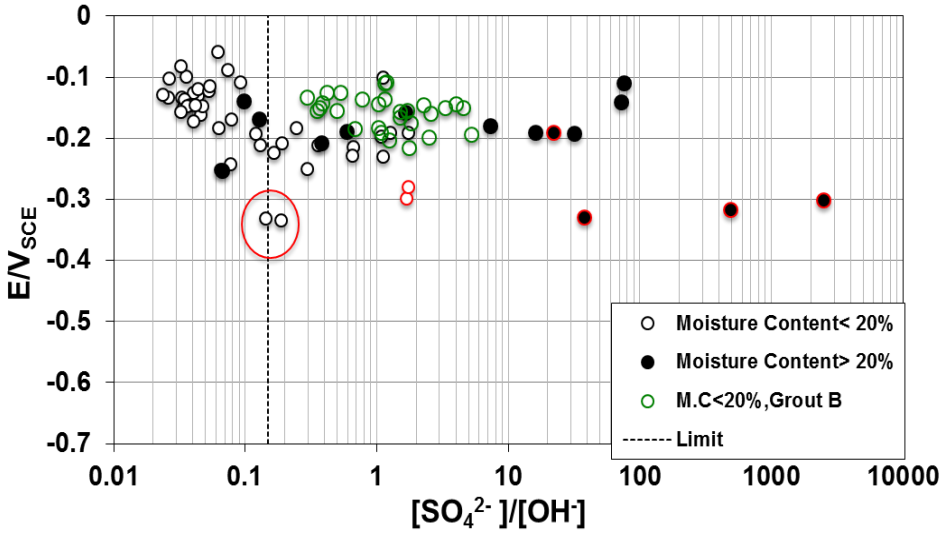
Med Sulfate, Low Chloride

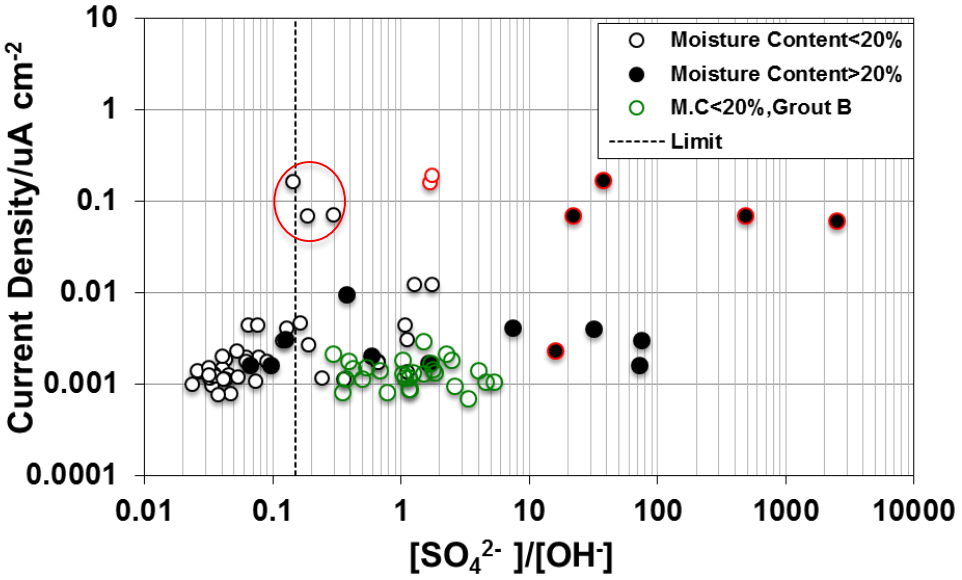
Low Sulfate, High Chloride

Med Sulfate, High Chloride

- Corrosion of steel in tee header typically with >~ 0.01 $g_{sulfate}$ / g_{powder}
- The steel in deficient grout with combined presence of sulfates with low level chlorides had active corrosion potentials <-400mV_{SCE} and current densities as high as 6 uA/cm^2.

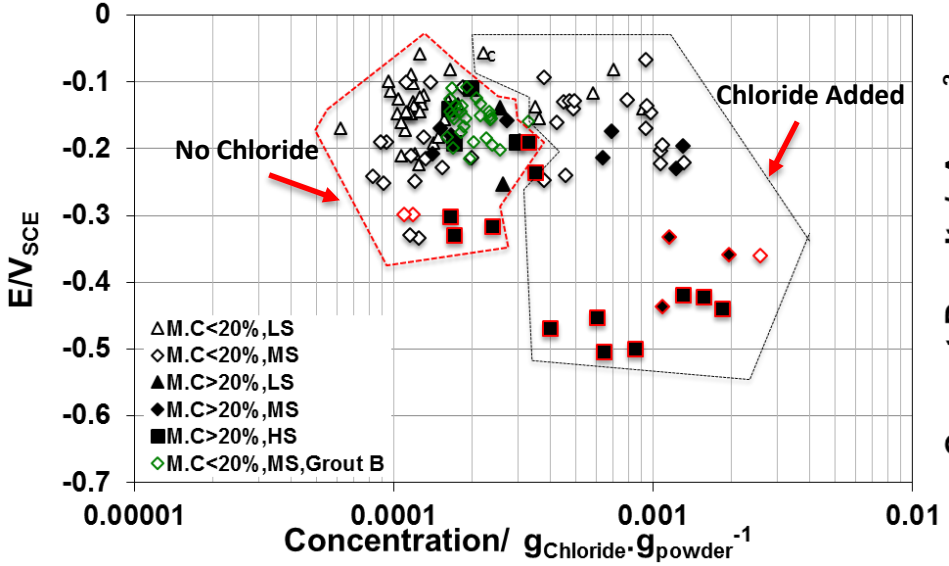
Recommendations for Sulfate Threshold Limits

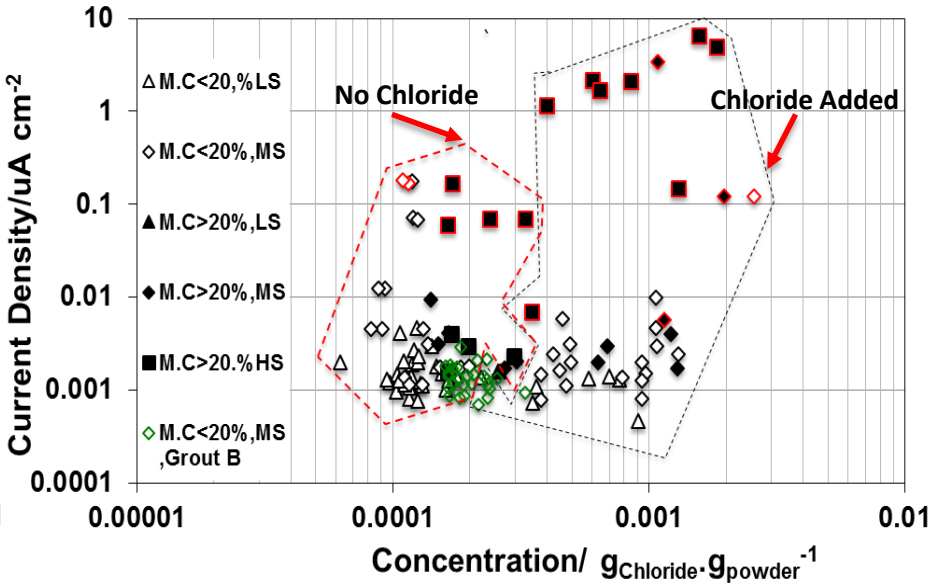




- Changes in pore water chemistry can affect the corrosion initiation in the presence of sulfate ions.
- Conservative threshold limit based on active corrosion conditions(E_{corr}< - 300 mV_{sce} and i_{corr} > 0.1 mA/cm^2)
- **[SO_4^{2-}]/[OH^-]=0.15 may be considered as a conservative limit.**

Recommendations for Sulfate Threshold Limits



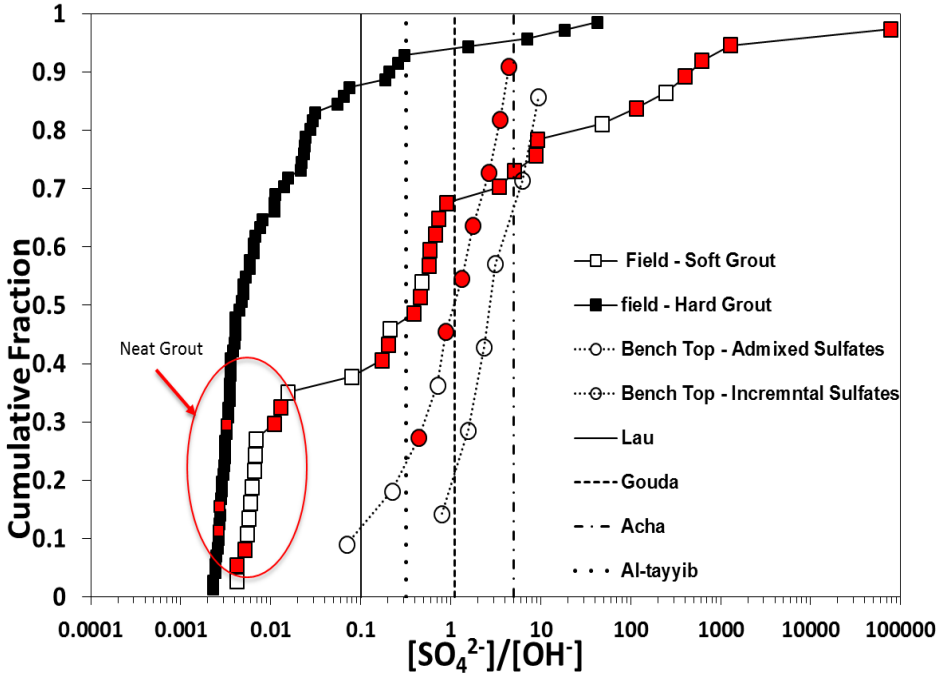


- Sulfate accumulation by segregation can cause corrosion initiation. However addition of low amount of chloride (0.08% by cement weight) can increase the corrosion rate.

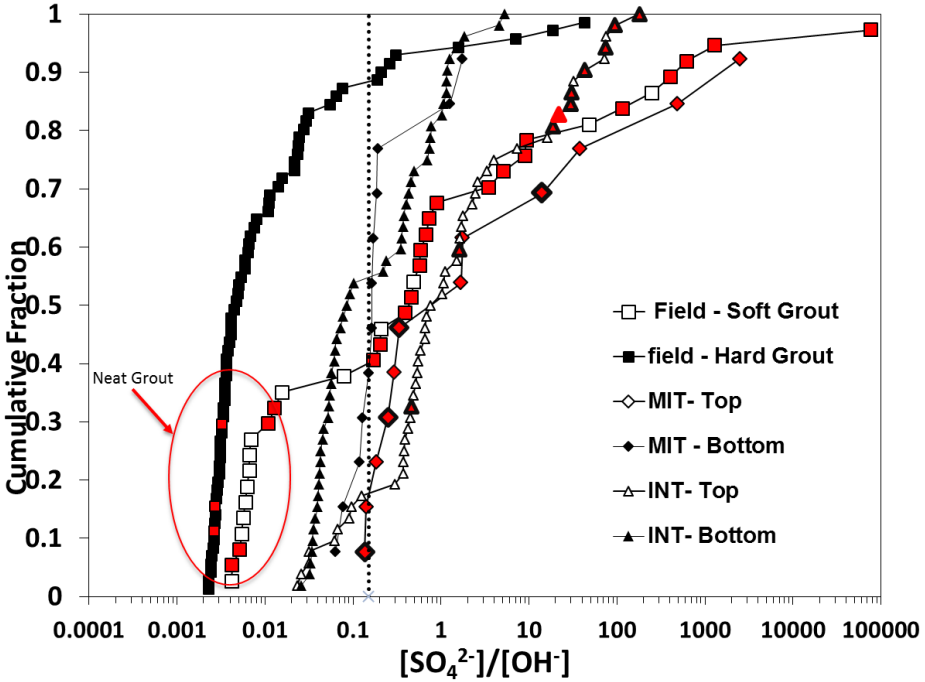
Low Sulfate (LS)<0.0004 $g_{sulfate}/g_{Powder}$
0.0004<**Med Sulfate (MS)** <0.01 $g_{sulfate}/g_{Powder}$,
High Sulfate(HS)>0.01 $g_{sulfate}/g_{Powder}$

Sulfate Threshold Values in Alkaline Environment

Solution Tests



MIT and INT



- Steel corrosion was observed in deficient grout when $[SO_4^{2-}]/[OH^-]$ >~ 0.15 in grout pore water.
- This range of sulfates corresponds to 600 ppm to 3000 ppm in pH range 12.6 to 13.3 in pore water solution. (The corresponding samples showing the conservative values had sulfate concentration 0.0007g/g).

- Comparable limits suggested for concrete durability in sulfate environment.

Conclusions

- The testing in alkaline solution showed **sulfates alone can initiate corrosion** in absence of chlorides
- **Grout segregation cause adverse pore water chemistry** and grout properties that reduce the tolerance and the threshold of the steel to aggressive ions.
- **Assessment of corrosion susceptibility in deficient grout by chloride values alone is insufficient** as sulfate ion presence and grout characteristics are also important.
- **$[SO_4^{2-}]/[OH^-]=0.15$** can be considered as a **conservative limit** for corrosion initiation of steel in grout. This limit can be converted to 600-3000 ppm sulfate in solution for pH 12.6-13.3. The limit also corresponded to sulfate content $0.0007 g_{Sulfate}/g_{grout}$.
- INT and MIT test methods can promote grout segregation and differentiate grout robustness to adverse mix conditions and identify corrosion activity

Acknowledgments

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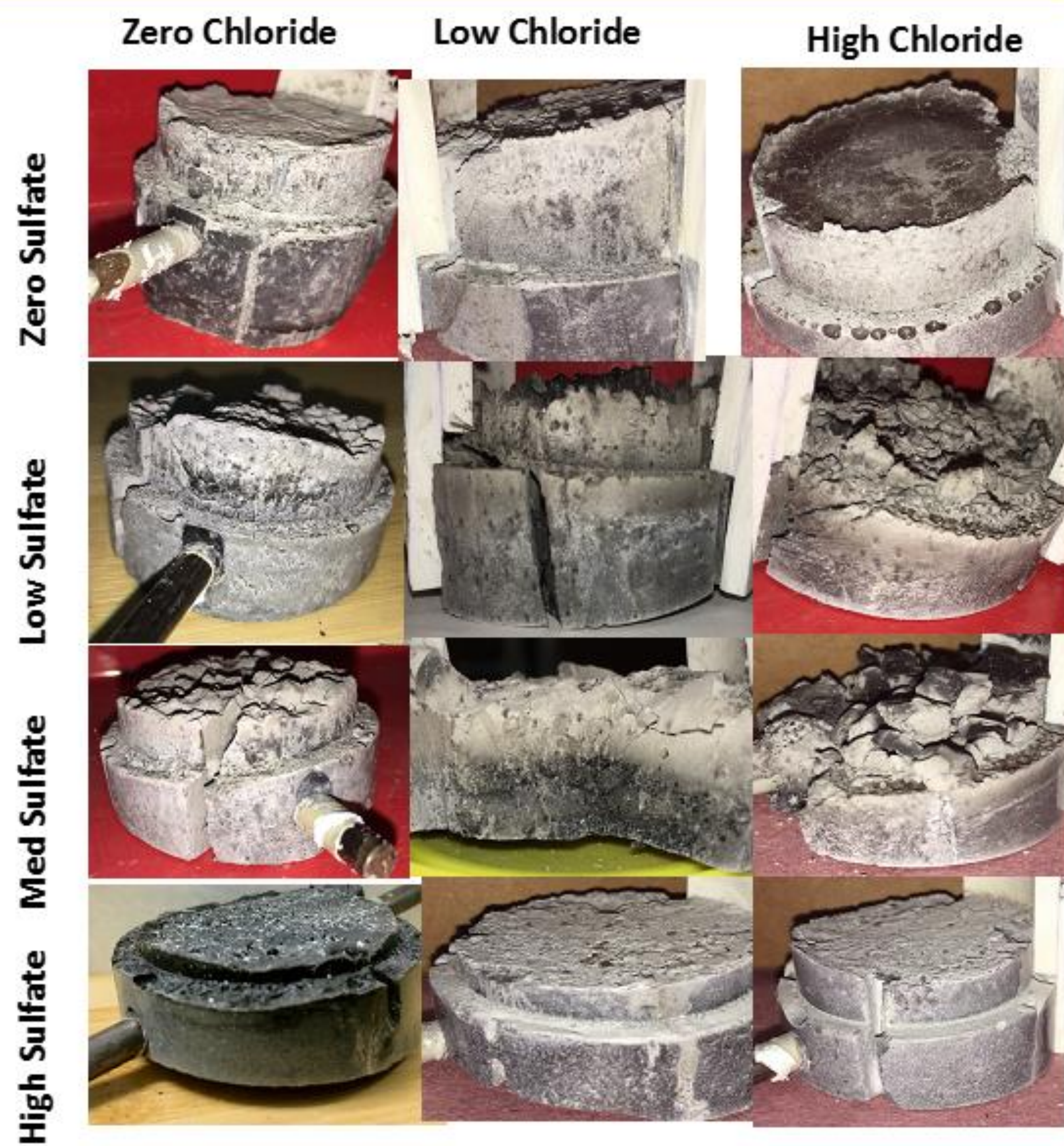
- Support from the FDOT State Materials Office and assistance by H.R. Hamilton in casting MIT samples is acknowledged here.

THANK YOU



Zero Chloride
Low Chloride
High Chloride
Zero Sulfate
Low Sulfate
Med Sulfate
High Sulfate