STP-NU-068

CORROSION OF A193 GRADE B7 BOLT MATERIAL IN BWR SODIUM PENTABORATE SOLUTIONS

ASME STANDARDS TECHNOLOGY, LLC

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FOREWORD

The effect of corrosion of typical Boiler Water Reactor (BWR) borated water system bolting used in stainless steel valve flanges installed in BWR sodium pentaborate systems has been recently questioned. A better understanding of BWR borated water system bolt corrosion will help determine whether BWR borated water is not as corrosive as PWR borated water. This report was undertaken to assess the use of A193 Grade B7 bolts in stainless steel flanges installed in a BWR sodium pentaborate systems. The research was conducted by NWT Corporation at the request of Electric Power Research Institute (EPRI).

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1 INTRODUCTION

To better determine the impacts of using A193 Grade B7 bolts in stainless steel flanges installed in a Boiler Water Reactor (BWR) sodium pentaborate (NaPB) systems, quantification of the corrosion rates of this material in NaPB solutions was investigated. Two types of tests were performed. First, coupons of 4140 (the base material for A193 Grade B7), C4340 low alloy steel, C1010 carbon steel and 410 stainless steel were immersed in a 12% NaPB solution at ~95°F and a 12 to 20% solution at ~185°F. An A193 Grade B7 bolt was also immersed in a 12% NaPB solution and in demineralized water at 95ºF. Coupons and bolts were intermittently examined and photographed, and weight change measurements were made to assess corrosion rates after three weeks and two months of exposure.

Second, tests to assess corrosion of A193 Grade B7 bolts when leakage occurs across stainless steel flange seal surfaces were performed. The test flanges had a 4-inch diameter and a bolt circle diameter of ~3 inches. Three flanges were exposed at ~99ºF, and one flange was exposed at ~203ºF. Leakage of the NaPB solution was simulated by injecting a 12 weight percent NaPB solution through a small diameter Teflon tube onto one of the four bolts in each flange at a rate of ~0.1 ml per minute. One flange was allowed to accumulate borate salts as a result of the leakage. The exterior surface of the other flange was brushed clean approximately every two weeks. The third 100ºF flange was insulated with NUKON™ and was not cleaned during the test period. The 203ºF flange was not insulated and was allowed to accumulate borate salts over the test period. Flanges were exposed for approximately two months.

After the nearly two month exposures, the flanges were disassembled, and the bolts and flanges were photographed and inspected. The bolts were rinsed of borate salts, weighed, de-scaled, and reweighed to determine metal loss. Local corrosion depths were estimated based on the weight losses.

Test methodology is summarized in Section 2. Coupon test results are summarized in Section 3. Flange bolt testing is summarized in Section 4.

2 TEST METHODOLOGY

2.1 Coupon Tests

Rectangular coupons of C1010 (carbon steel), C4340 and C4140 low alloy steel and 410 stainless steel were exposed at static conditions to a sodium pentaborate solution with an initial concentration of 12% at temperatures of ~ 95ºF and 185ºF. 4140 is the base material for the A193 Grade B7 bolts. The other materials were selected since their corrosion behavior in PWR boric acid solutions had been previously evaluated [1][2]. The coupons were intermittently removed for inspection and weighing to assess corrosion.

Composition of the coupons is shown in Figure 2-2 [3]. Dimensions are shown in Figure 2-1. Total area of each coupon was ~3 in^2 or 0.194 dm^2. The coupons were finished using a 120 grit belt prior to exposure [3]. The pH and conductivity of the 12% NaPB solution at ~25ºC were 7.08 and 11,600 µS/cm, respectively.

Coupons were cleaned with acetone and weighed before testing. Four coupons of each alloy were suspended by nylon lines in separate 800 ml glass beakers and covered with polycarbonate sheet for testing during the 95ºF tests. A similar approach was used for the tests at 185ºF except the beakers were polycarbonate. The coupons were completely submerged in the 12% NaPB solution. Solutions were air saturated. Coupons were visually inspected, dried and weighed after approximately 20 days and also after two months of exposure.

The NaPB solution concentration remained at 12% throughout the tests at 95ºF since evaporative water losses were minimal. However, water losses during the 185ºF tests were significant, and solution losses were initially compensated for by adding a 12% NaPB solution. This led to an increase in the solution NaPB concentration from 12% to ~18% over the first 10 days of testing. At that time, the solution concentration was adjusted to 12%, and demineralized water was subsequently added to compensate for water losses. The solution concentration remained at 12% for the remainder of the exposures.

Figure 2-1: Coupon Design

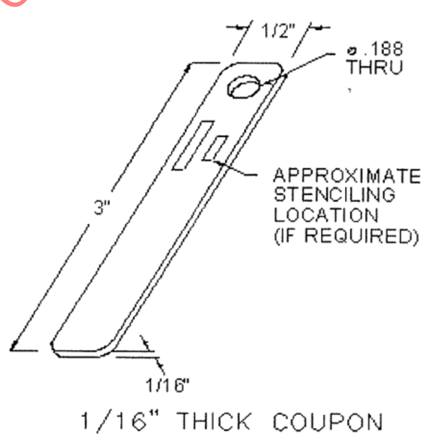


Figure 2-2: Coupon and Bolt Material Composition

	C4140	C4340	410	C1010	A193 Grade B7
C	0.41	0.43	0.14	0.13	0.37-0.49
Mn	0.9	0.7	0.36		.65-1.1
P	0.019	0.01	0.025	99.62	0.035
S	0.015	0.003	0.001	0.6	0.04
Si	0.22	0.23	0.39	0.04	.15-.35
Cu	0.22	0.14	0.15		
Ni	0.15	1.75	0.19	0.05	
Cr	1	0.75	12.17		.75-1.2
Mo	0.21	0.25	0.03		.15-.25
Al	0.026	0.004	0.002		
V	0.006	0.045			
Nb		0.007			
Sn			0.01		
Ni			0.01		

2.2 Flange Tests

Four A193 Grade B7 bolts were installed in each 304 stainless steel 4-inch diameter flange. Leakage was simulated by injecting a 12% NaPB solution through a 1/16-inch ID Teflon tube onto the threaded section of one bolt at the flange seal interface. The solution was injected at a rate of approximately 0.1 ml/minute (liquid velocity of 0.003 ft/second at injection tube exit). Bolt dimensions are shown in Figure 2-3. A flange schematic is shown in Figure 2-4. The test configuration is shown in Figure 2-5.

Three flanges were exposed at ~95ºF. Two of these flanges were not insulated. One of these flanges was allowed to accumulate borate salts that developed as a result of leakage. The other uninsulated flange was cleaned approximately every two weeks. The third 95ºF flange was insulated with NUKON™ and was allowed to accumulate borate salts over the test period. One flange was exposed at ~203ºF. This flange was not insulated and was allowed to accumulate borate salts over the test period. Total exposure time of all flanges was ~55 days. The flanges were then disassembled, the bolts were visually inspected and the extent of corrosion assessed based on the inspection results and weight loss measurements.

Figure 2-3: A193 Grade B7 Bolt Dimensions

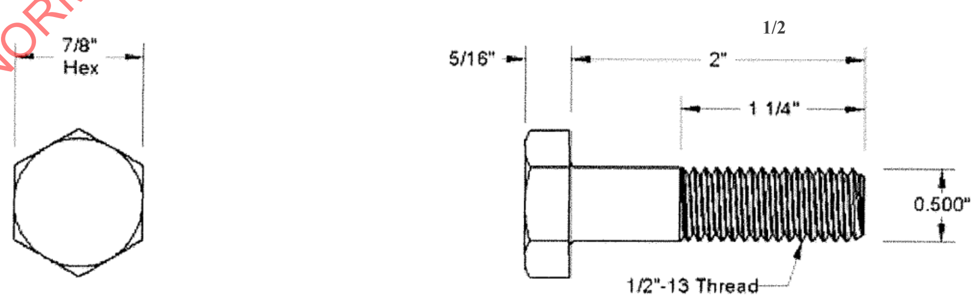


Figure 2-4: Schematic of Flange Configuration

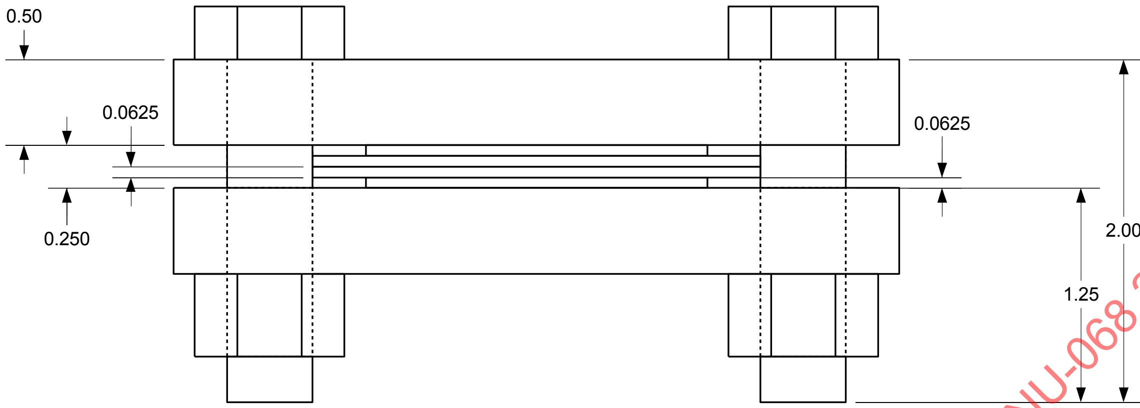


Figure 2-5: Flange Test Configuration

3 COUPON TESTING

3.1 Coupon Tests at ~95ºF

3.1.1 Visual Observations

Coupon tests at ~95ºF of C1010 (carbon steel), C4340 and C4140 low alloy steels and 410 stainless steel were initiated on May 31, 2013. Four coupons of each alloy were suspended by nylon lines in separate 800 ml glass beakers covered with polycarbonate sheet. Beakers were placed in a stainless steel oven. The coupons were completely submerged in 12% NaPB solutions which were air saturated. Temperature was measured with a calibrated thermocouple immersed in a polystyrene flask filled with water and located in the center of the oven.

Visual observations of the coupons submerged in the glass beakers indicated minimum corrosion of all materials throughout the exposure period. All solutions remained clear. Coupons were initially removed for inspection on June 20 after ~20 days of exposure. Coupons were rinsed with demineralized water (~0.1 μS/cm) and then air dried for several hours before visual inspection, photographing and weighing. There was no visible indication of corrosion of the C4310 low alloy steel or 410 stainless steel coupons.

The condition of the C1010 test coupons (Numbers 1 to 4) is compared to that of an un-exposed C1010 coupon (Number 7) in Figure 3-1. Very limited indications of localized corrosion are present near the bottom of Coupon 1. Condition of the C4140 test coupons (Numbers 7 to 10) is compared to that of an un-exposed C4140 coupon (Number 11) in Figure 3-2 Figure 3-3. The only visually observable corrosion of the C4140 material was on Coupons 8 and 10. Coupon 10 exhibited small localized regions of oxide formation on the front side of the coupon. Coupon 8 exhibited more limited localized corrosion on the lower end of the back side of the coupon.

Figure 3-1: C1010 Test Coupons 1, 2, 3 and 4

After 20 Days of Exposure and Un-Exposed Coupon 7

Figure 3-2: C4140 Test Coupons 7, 8, 9 and 10 (Front Face)
After 20 Days of Exposure and

Figure 3-3: C4140 Test Coupons 7, 8, 9 and 10 (Back Face)
After 20 Days of Exposure and Un-exposed Coupon 11

After inspection and weighing on June 20, the coupons were returned to the beakers in which they were initially exposed and replaced in the oven to continue exposure at ~95°F. Visual observations of the coupons submerged in the glass beakers throughout the second exposure period again indicated minimal corrosion of all materials. All solutions remained clear. Coupons were removed for final inspection and weighing on August 23 after a total of ~2 months of exposure. Coupons were rinsed with demineralized water (~0.1 µS/cm) and then air dried for several hours before visual inspection, photographing and weighing.

Visual observations after the 20 day and 2 month exposures are summarized in Figure 3-7. There was no observable corrosion of the C4340 or 410 materials. Limited localized corrosion was observed on one of the four C1010 carbon steel coupons and three of the four C4140 coupons. Small regions of oxide/hydroxide discoloration were present over varying fractions of the coupon surfaces. Examination under a microscope indicated that a shallow pit with a diameter in the range of 10 to 20 microns was present at the center of the discolored regions. The extent of corrosion varied from the back to the front side of the coupons. For example, the front surface of C4140 coupon 10 had small areas of oxide discoloration over the entire front surface of the coupon but no regions of discoloration apparent on the back side. The area around the discolored regions was relatively shiny and free of corrosion.

3.1.2 Weight Measurements

After rinsing and drying, each coupon was weighed, and the changes in weight at the end of each exposure period were determined. Coupon weight losses and the estimated corrosion rates expressed as milligrams of weight loss per dm^2 per month (mg/dm^2-month) are given in Figure 3-8. Results are also shown in Figure 3-4, Figure 3-5 and Figure 3-6. The total coupon area (0.194 dm^2) was used for this calculation. Note that the corrosion rate calculated in this manner is an average value for the total coupon surface and is based on the assumption that 100% of the oxidized material is released to the solution. Observations of coupon weight gains (negative values of weight loss) indicate that a portion of the oxide formed during the corrosion process was retained on the surface.

Most coupons exhibited a weight loss indicating metal release to the solution during the initial 20 days of exposure. There was considerable variability in the results of individual coupons of a given material. After two months of exposure, the coupon weights were generally very similar to those of the initial non-exposed coupons. Weight losses (or gains) after two months were all <5 mg/dm^2-month. To put this value into perspective, a metal release rate of ~160 mg/dm^2-month corresponds to a metal loss rate of ~1 mil/year for these materials. The C4140 material (which is the base material for the A193 Grade B7 bolts) had a weight increase of ~1 mg/dm^2-month after the two month exposure.

General corrosion of all of the materials over the two month exposure period was minimal based on the visual inspection results and weight change measurements.

Figure 3-4: Effect of Exposure Time on Coupon Weight Change
(12% Sodium Pentaborate Solution at 95°F)

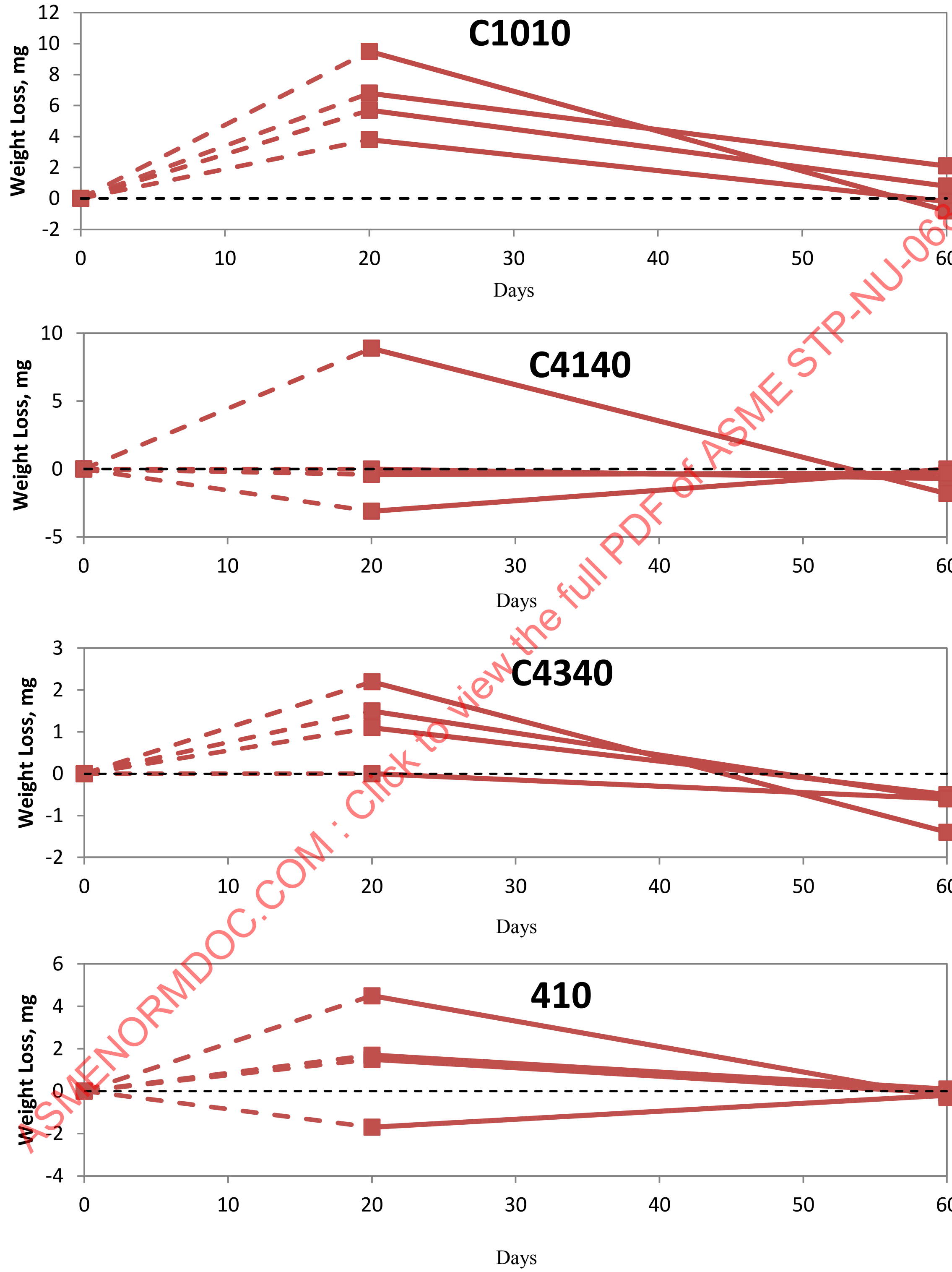


Figure 3-5: Effect of Exposure Time on Coupon Weight Change per Unit Area (12% Sodium Pentaborate Solution at 95°F)

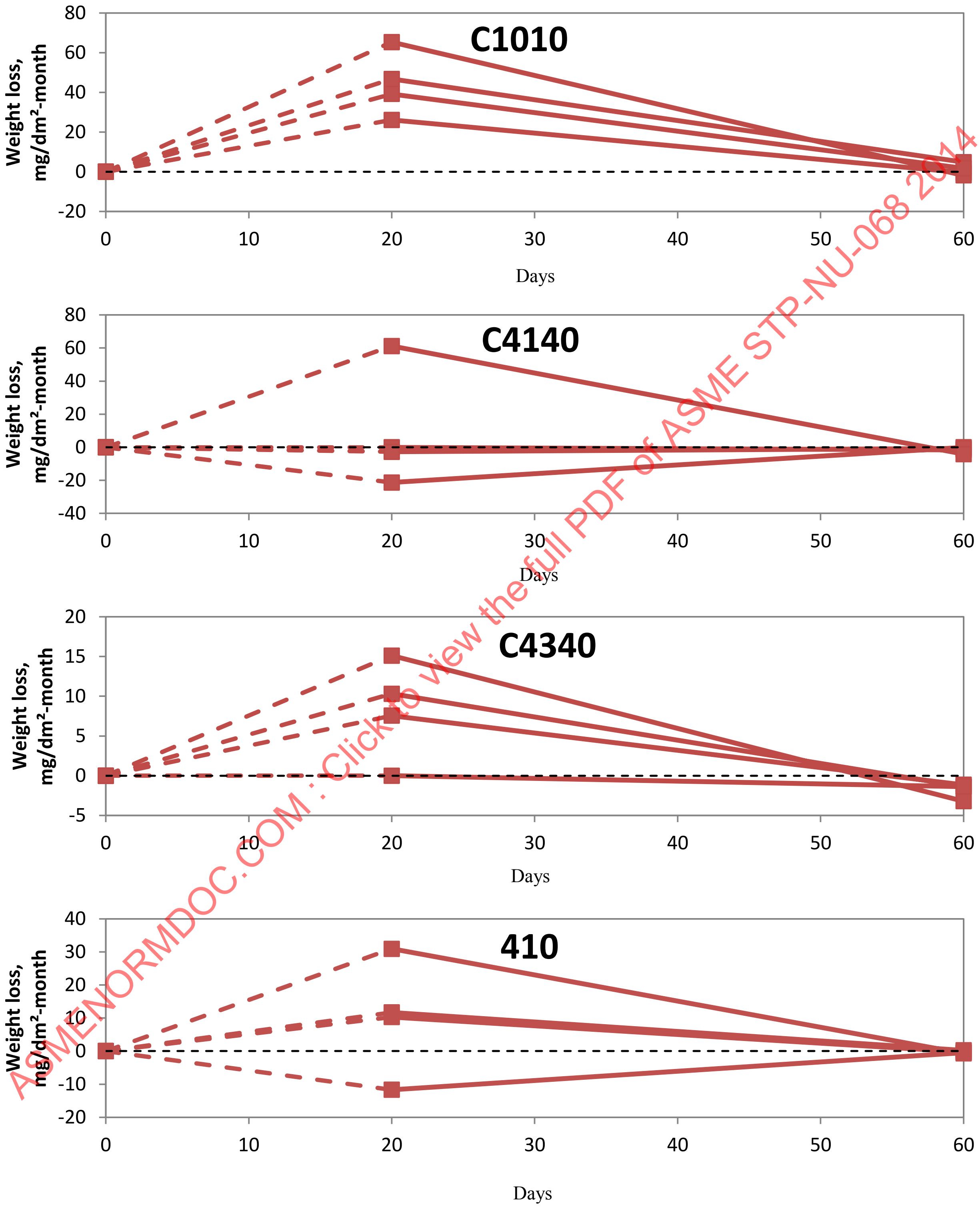
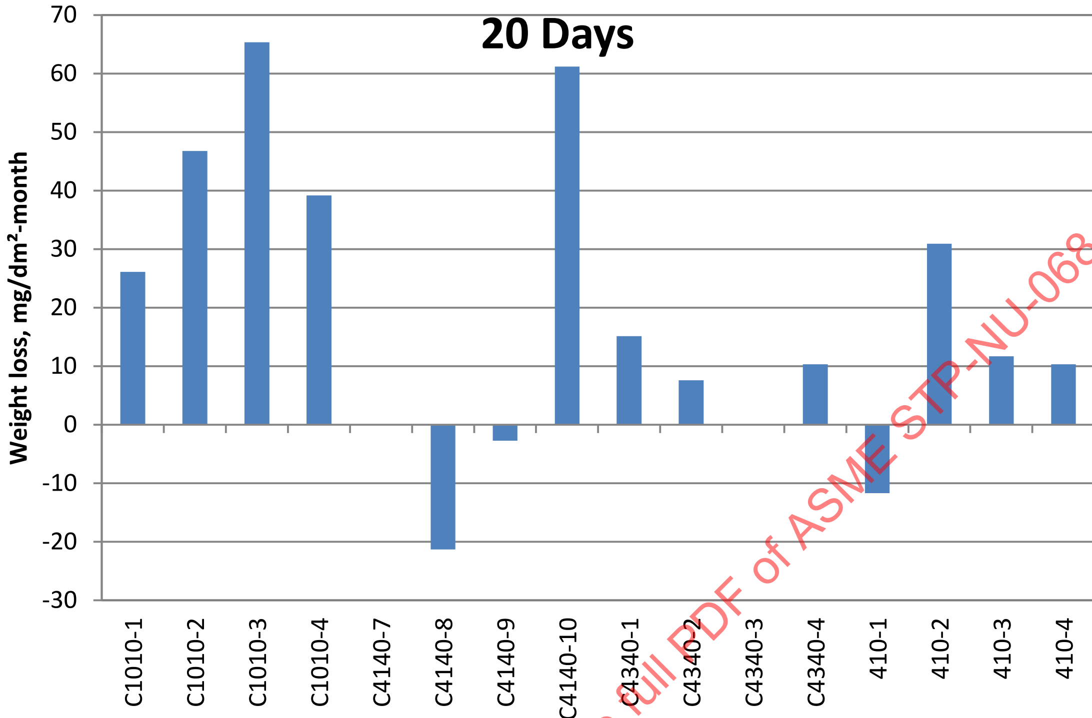


Figure 3-6: Effect of Exposure Time on Coupon Weight Change per Unit Area (12% Sodium Pentaborate Solution at 95°F)



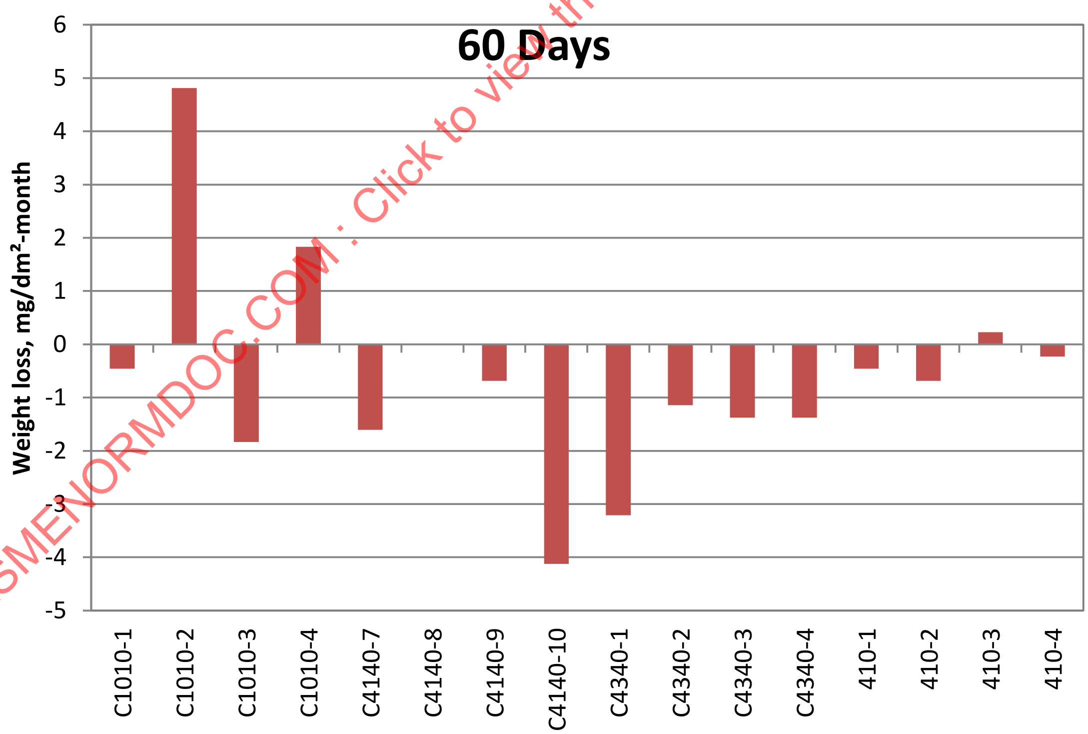


Figure 3-7: Visual Observations of Coupons Exposed to 12% Sodium Pentaborate Solutions at 95°F

Coupon Series		20 Day Exposure		2 Month Exposure	
	Coupon No.	**Photo ID**	**Observations**	**Photo ID**	**Observations**
C1010	2-4	N/A	No visible corrosion; shiny surface	N/A	No visible corrosion; shiny surface
C1010	1	C1010	Small of regions of oxide discoloration on bottom 10% of front side	C1010 Front	Slight increase in number of oxide nodules on bottom 10% of front side. No nodules on back side
C4140	7	N/A	No visible corrosion	C4140 Back	Limited number of oxide nodules on bottom of back side
C4140	8	C4140 Back	Limited regions of oxide discoloration on bottom back side	C4140 Back and Front	Limited oxide nodules on bottom 10% of front side. Limited oxide nodules on bottom 40% of back side
C4140	9	N/A	No visible corrosion; shiny surface	C4140 Back	No visible corrosion; shiny surface
C4140	10	C4140	Limited number of regions of oxide discoloration on front side	C4140 Front	Oxide nodules over entire front surface. No nodules on back side
C4340	1-4	N/A	No visible corrosion; shiny surface	N/A	No visual corrosion; shiny surface
410	1-4	N/A	No visible corrosion; shiny surface	N/A	No visible corrosion; shiny surface

Figure 3-8: Coupon Weight Changes after 20 and 60 Day Exposure to 12% Sodium Pentaborate Solution at 95°F

Alloy	S/N	Weight, g			Weight loss, mg		Weight loss, mg/dm²-mo	
		0 days	20 days	60 days	20 days	60 days	20 days	60 days
C1010	1	10.6694	10.6656	10.6696	3.8	-0.2	26.1	-0.5
C1010	2	10.5072	10.5004	10.5051	6.8	2.1	46.7	4.8
C1010	3	10.6370	10.6275	10.6378	9.5	-0.8	65.3	-1.8
C1010	4	10.8465	10.8408	10.8457	5.7	0.8	39.2	1.8
C4140	7	14.1215	14.1215	14.1222	0	-0.7	0.0	-1.6
C4140	8	14.3101	14.3132	14.3101	-3.1	0	-21.3	0.0
C4140	9	14.2528	14.2532	14.2531	-0.4	-0.3	-2.7	-0.7
C4140	10	14.2675	14.2586	14.2693	8.9	-1.8	61.2	-4.1
C4340	1	12.3828	12.3806	12.3842	2.2	-1.4	15.1	-3.2
C4340	2	12.5615	12.5604	12.5620	1.1	-0.5	7.6	-1.1
C4340	3	12.6120	12.6120	12.6126	0	-0.6	0.0	-1.4
C4340	4	12.5844	12.5829	12.5850	1.5	-0.6	10.3	-1.4
410	1	10.3230	10.3247	10.3232	-1.7	-0.2	-11.7	-0.5
410	2	10.1903	10.1858	10.1906	4.5	-0.3	30.9	-0.7
410	3	10.1710	10.1693	10.1709	1.7	0.1	11.7	0.2
410	4	10.2213	10.2198	10.2214	1.5	-0.1	10.3	-0.2

3.2 Bolt Exposure at 95ºF

When it became apparent that the C4140 coupons were exhibiting minimal corrosion in the 12% NaPB solution at 95ºF, an A193 Grade B7 bolt was suspended in a 600 ml beaker containing a 12% NaPB solution. A second bolt was suspended in a beaker containing demineralized water, and the beakers placed in the coupon exposure oven. After only one day, a rust colored oxide film had formed on the bolt in the demineralized water, and the solution had become discolored. No corrosion of the bolt in the NaPB solution was observed. After several days of exposure, the demineralized water solution was rust-colored indicating formation and release of hydrated iron oxides. The NaPB solution remained clear.

The bolts were removed for inspection after two months of exposure. After drying the bolts, they were weighed, rinsed with demineralized water, reweighed, brushed, rinsed again and reweighed. The rinse solutions were filtered through a 0.22 micron filters which were then dried and weighed. Results are summarized in Figure 3-9. There was no measurable corrosion of the bolt submerged in the 12% NaPB solution. However, the bolt submerged in demineralized water had a weight loss of approximately 180 mg/dm^2-month corresponding to a metal loss of approximately 1.1 mils per year. The bolt surface area was estimated to be 0.40 dm^2.

The total amount of iron oxide/hydroxide collected by filtering the rinse solutions from the demineralized water bolt was ~0.189 mg. This corresponds to a metal release of 0.119 grams (assuming that the iron was present as FeOOH) compared to a measured weight loss of ~0.142 grams. The amount of material collected by filtration of the rinse solutions for the bolt suspended in the NaPB solution was near the detection level.

Figure 3-9: Table 3:1 Corrosion of A193 Grade B7 Bolts during Two Month Exposure at 95°F

Bolt ID	**9**	**7**
Solution	**Deionized Water**	**12% Sodium Pentaborate**
Initial Weight, g	66.5085	66.4271
Dry Weight after exposure, g	66.4033	66.4299
Weight change, g	-0.1052	+0.0028
Weight after brushing, g	66.3669	66.4271
Oxide Removed by brushing, g	0.0364	0.0028
Total Metal Loss, g	0.1416	0
Weight Loss, mg/dm^2-mo*	180	~0
Collected Oxide/Hydroxide, g	0.1890	0.0013
Collected Metal Based on FeOOH, g	0.119	0.001

*Estimated bolt area of 0.40 dm^2

3.3 Coupon Tests at ~185°F

3.3.1 Visual Observations

Coupon tests of C1010 (carbon steel), C4340 and C4140 low alloy steels and 410 stainless steel at 185°F in NaPB solutions were initiated on June 25, 2013. Four coupons of each alloy were suspended by nylon lines in separate 800 ml polycarbonate beakers covered with a polycarbonate sheet to minimize evaporation. Beakers were placed in a stainless steel oven. The coupons were initially submerged in 12% NaPB solutions which were air saturated. Temperature was measured with a calibrated thermocouple immersed in a polystyrene flask filled with water and located in the center of the oven and by a thermocouple in the oven atmosphere. Evaporative losses from the beakers during the 185°F tests were significant. These losses were initially compensated for by addition of a 12% NaPB solution. This led to an increase in the NaPB concentration from 12% to ~18% over the first 10 days of testing. At that time, the solution concentration was adjusted to 12%, and demineralized water was subsequently added to compensate for water losses. The solution concentration remained at 12% for the remainder of the test.

Visual observations of the coupons throughout the exposure indicated minimum corrosion of all materials. All solutions remained clear. Coupons were initially removed for inspection on July 17 after ~22 days of exposure. They were rinsed with demineralized water (~0.1 µS/cm) and then air dried for several hours before visual inspection and weighing. There was no visual indication of corrosion on any of the coupons, and the coupons were not photographed. They were again removed after two months of exposure, weighed, visually inspected and photographed (Figure 3-7 to Figure 3-10). There were no indications of general or localized corrosion on the surfaces of any of the materials. However, there was a slight dulling of the C4140 coupon surfaces.

3.3.2 Weight Measurements

After rinsing and drying, each coupon was weighed, and the changes in weight during each exposure period were determined. Coupons were not descaled. After the initial exposure period, visual inspection and weighing, the coupons were returned to the same test beaker which contained the original NaPB solution. Coupon weight losses and estimated corrosion rates expressed as milligrams of weight loss per dm^2 per month (mg/dm^2-mo) are given in Figure 3-14. Results are graphically summarized in Figure 3-11, Figure 3-12 and Figure 3-13. The total coupon area (0.194 dm^2) was used for this calculation. Note that the corrosion rate calculated in this manner is an average value for the total coupon surface and is based on the assumption that 100% of the oxidized material is released to the solution. Observations of coupon weight gains (negative values of weight loss) indicate that a portion of the oxide formed during the corrosion process has been retained on the surface.

Most coupons exhibited a weight gain during the initial 20 days of exposure. After two months of exposure, the coupon weights were generally very similar to those of the initial non-exposed coupons. Weight losses (or gains) were all <2 mg/dm^2-month. To put this value into perspective, a metal release rate of ~160 mg/dm^2-month corresponds to a metal loss rate of ~1 mil/year for a material such as carbon steel.

Based on the visual inspection results and weight change measurements, general and localized corrosion of all test materials was minimal in the 185°F NaPB solution.

Figure 3-10: C410 Test Coupons 5, 6, 7 and 8 after Two Months of Exposure

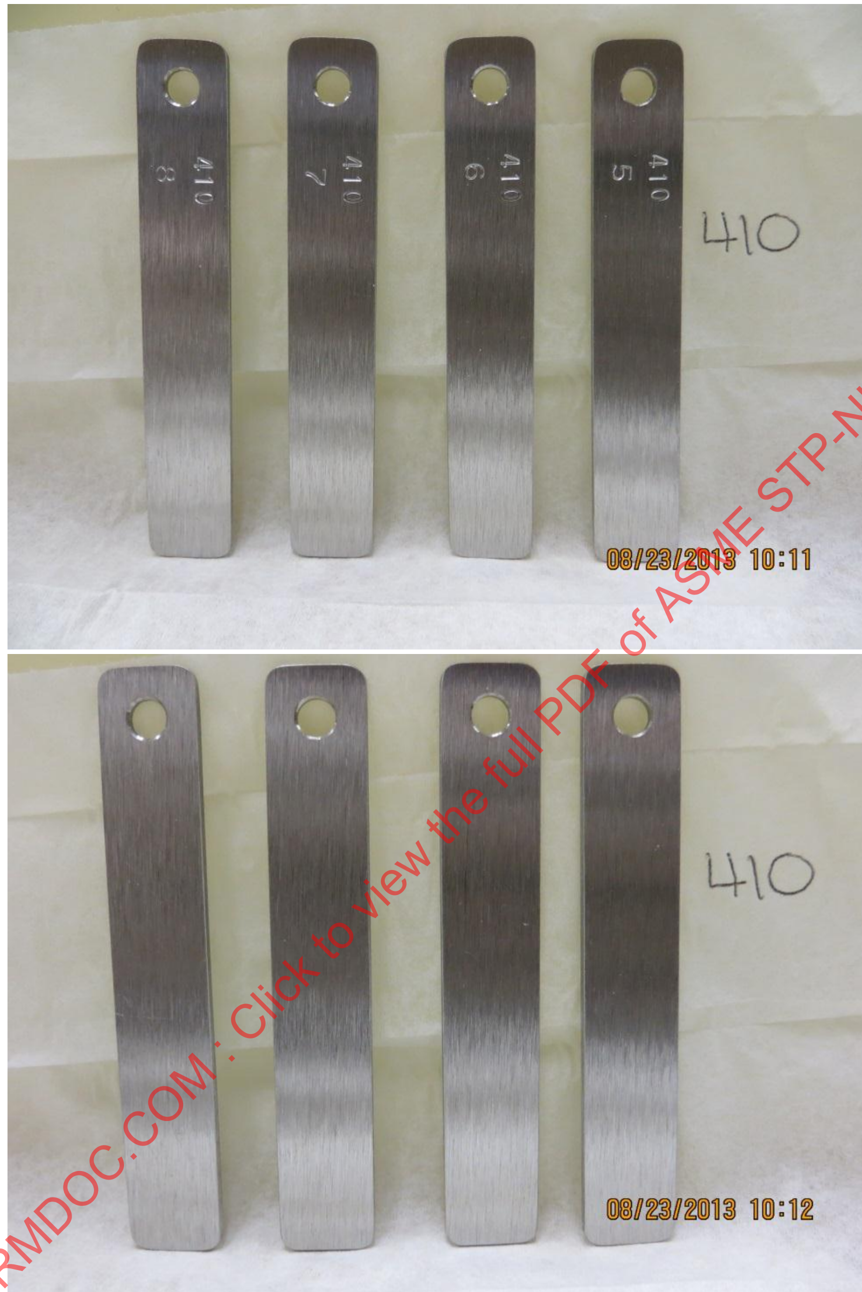


Figure 3-11: C1010 Test Coupons 5, 6, 7 and 8 after Two Months of Exposure

Figure 3-12: C4140 Test Coupons 11, 12, 13 and 14 after Two Months of Exposure

Figure 3-13: C4340 Test Coupons 5, 6, 7 and 8 after Two Months of Exposure

Figure 3-14: Coupon Weight Changes after Exposure to Sodium Pentaborate Solution at 185°F

Alloy	Serial Number	Weight, g			Weight loss, mg		Weight loss, mg/dm²-mo	
		t = 0 days	t = 22 days	t = 60 days	t = 22 days	t = 60 days	t = 22 days	t = 60 days
C4340	5	12.6504	12.6506	12.6504	-0.2	0	-1.4	0.0
C4340	6	12.5832	12.5829	12.5830	0.3	0.2	2.1	0.5
C4340	7	12.6568	12.6569	12.6571	-0.1	-0.3	-0.7	-0.7
C4340	8	12.4463	12.4464	12.4464	-0.1	-0.1	-0.7	-0.2
410	5	10.2096	10.2093	10.2094	0.3	0.2	2.1	0.5
410	6	10.1389	10.1389	10.1390	0	-0.1	0.0	-0.2
410	7	10.1260	10.1260	10.1255	0	0.5	0.0	1.1
410	8	10.2494	10.2497	10.2490	-0.3	0.4	-2.1	0.9
C1010	5	10.8115	10.8127	10.8114	-1.2	0.1	-8.2	0.2
C1010	6	10.7481	10.7501	10.7486	-2	-0.5	-13.7	-1.1
C1010	7	10.8357	10.8371	10.8361	-1.4	-0.4	-9.6	-0.9
C1010	8	10.7273	10.7300	10.7273	-2.7	0	-18.6	0.0
C4140	11	14.2563	14.2584	14.2564	-2.1	-0.1	-14.4	-0.2
C4140	12	14.2200	14.2220	14.2207	-2	-0.7	-13.7	-1.6
C4140	13	14.3101	14.3129	14.3105	-2.8	-0.4	-19.2	-0.9
C4140	14	14.3419	14.3436	14.3420	-1.7	-0.1	-11.7	-0.2

Figure 3-15: Effect of Exposure Time on Coupon Weight Loss

(12% Sodium Pentaborate Solution at 185°F)

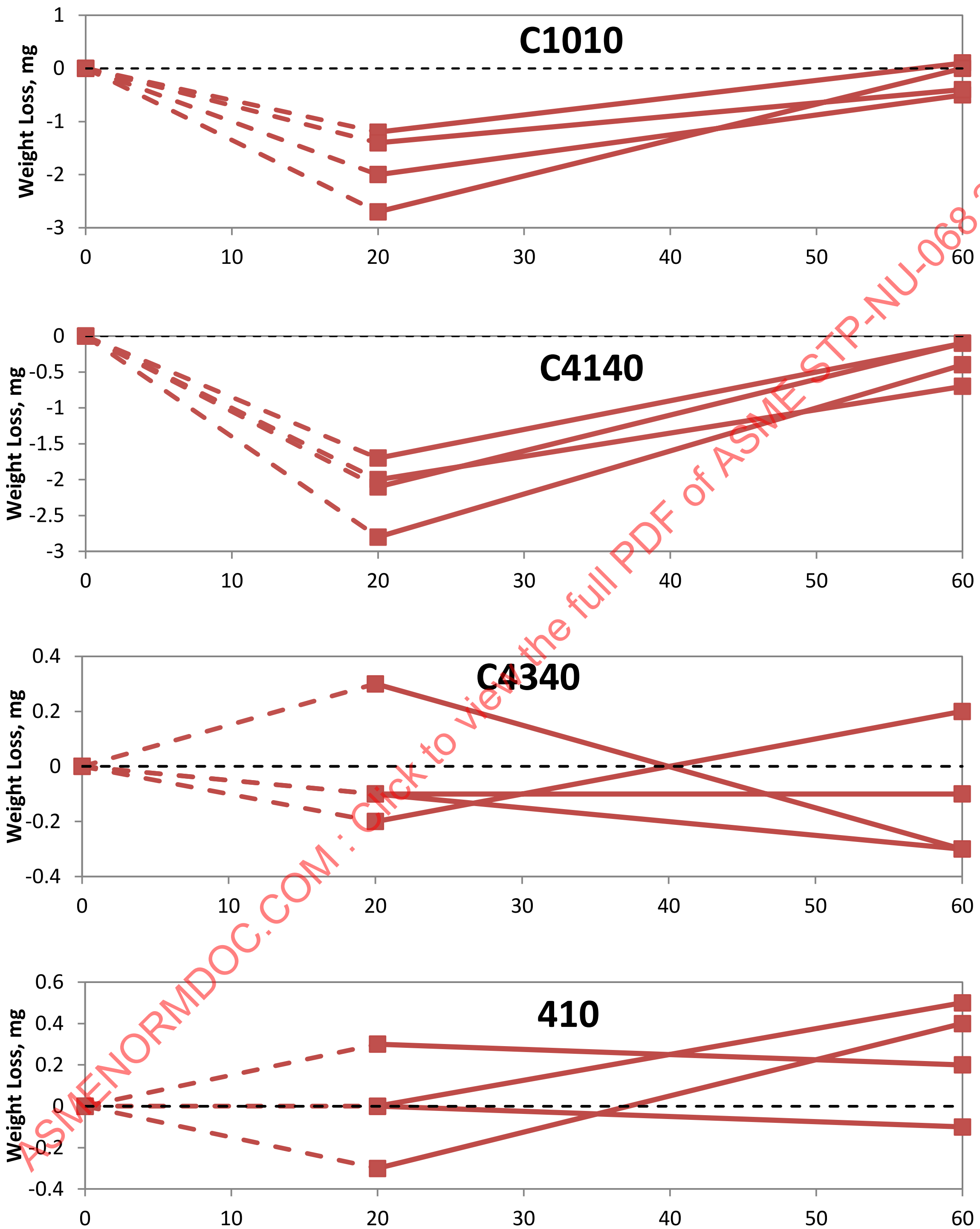


Figure 3-16: Effect of Exposure Time on Coupon Weight Loss per Unit Area
(12% Sodium Pentaborate Solution at 185°F)

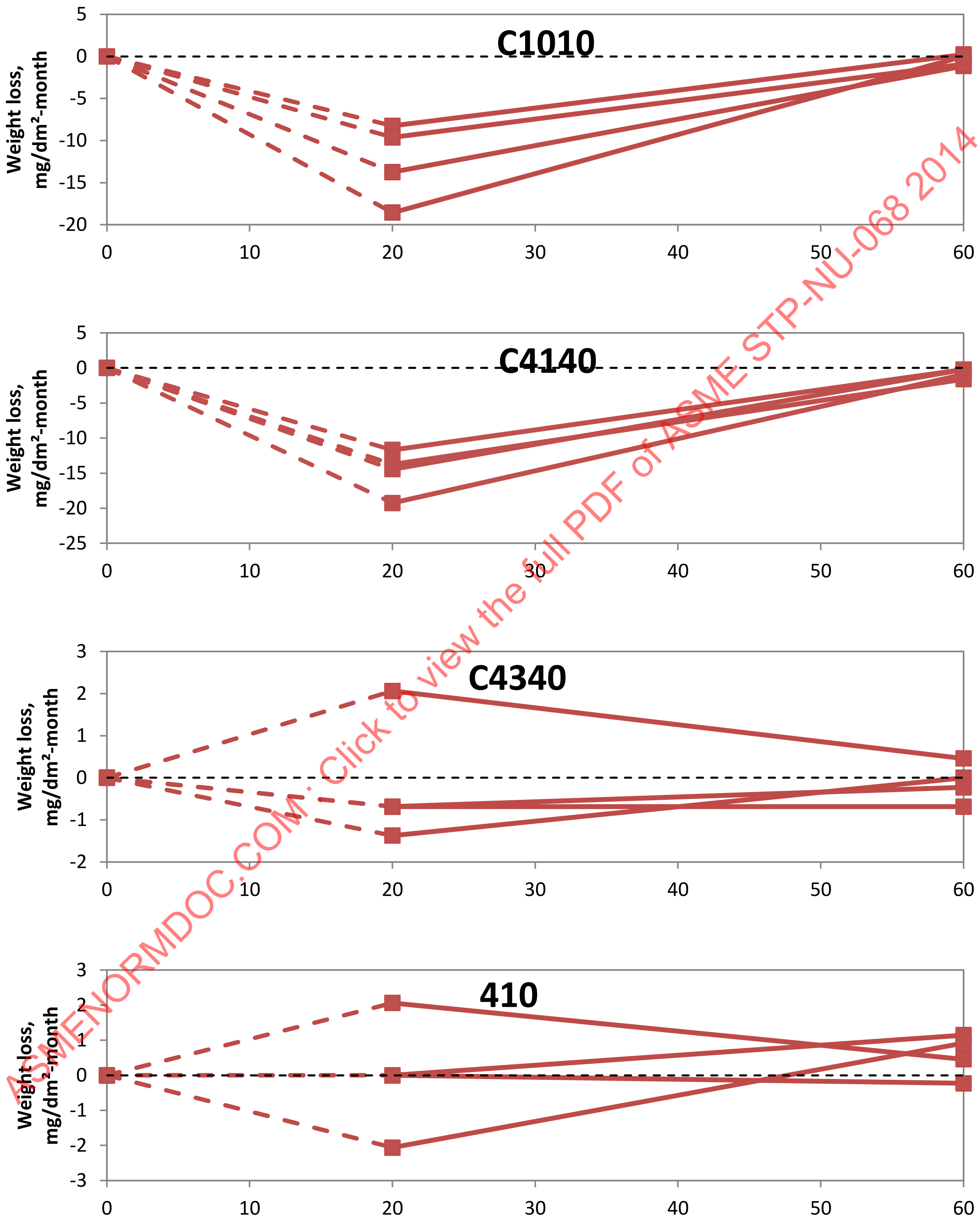
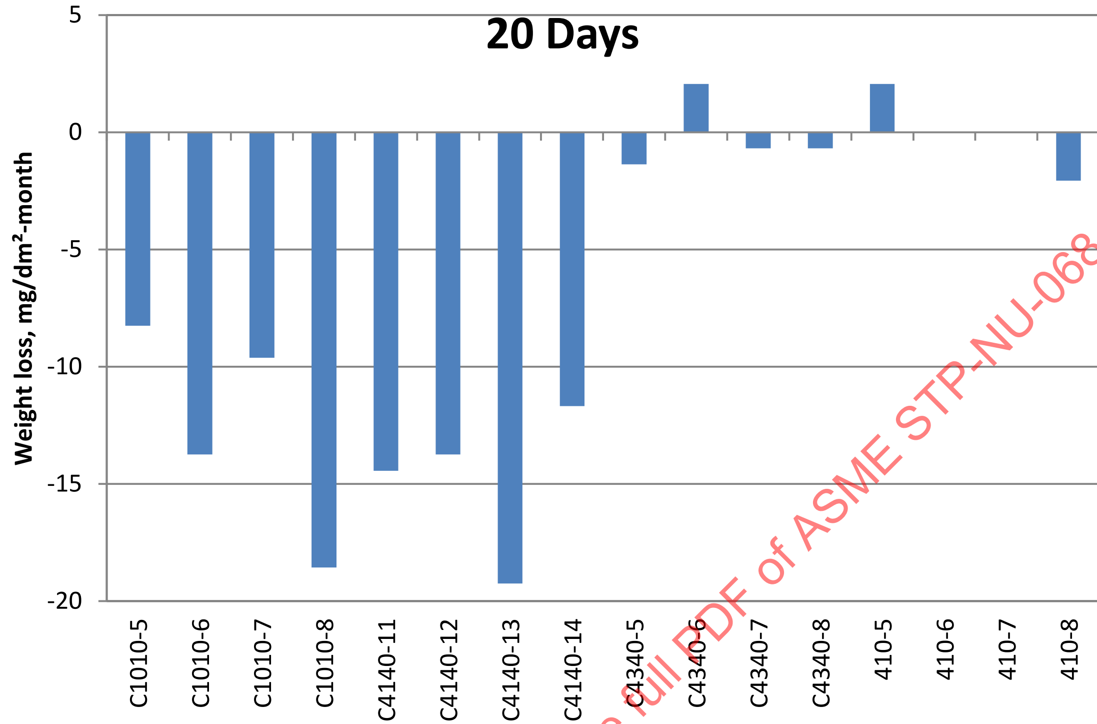
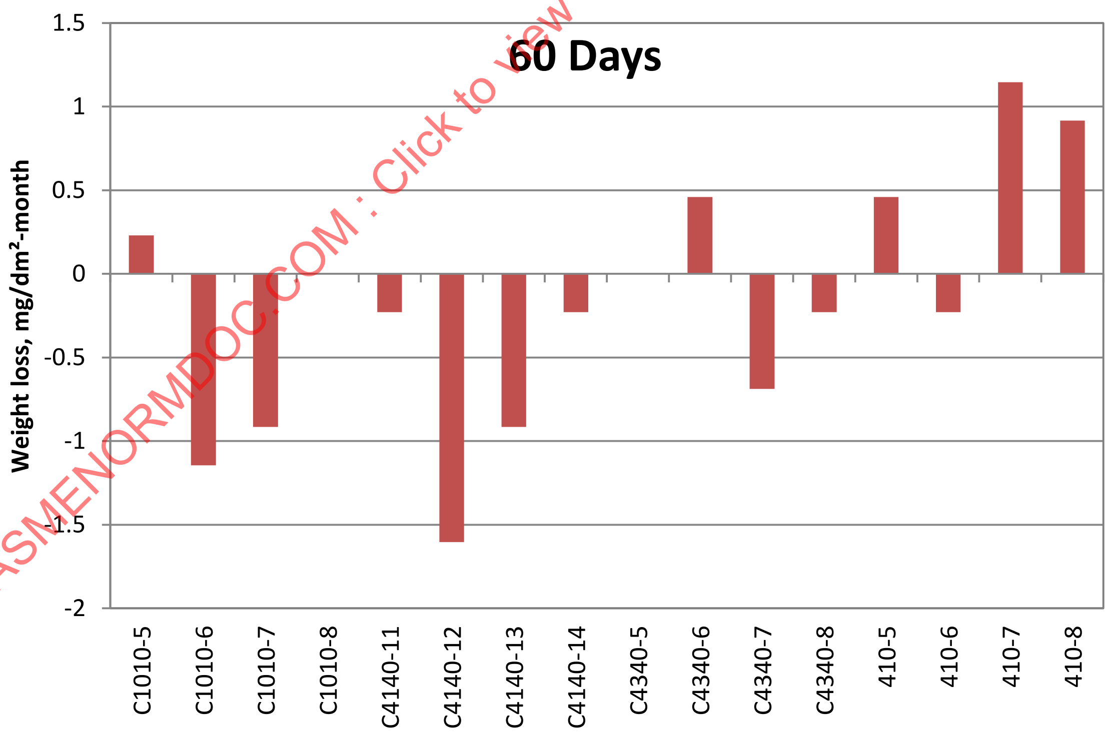


Figure 3-17: Effect of Exposure Time on Coupon Weight Change per Unit Area (12% Sodium Pentaborate Solution at 185°F)





4 FLANGE TESTS

4.1 Flange Tests at ~99°F

The test flange configuration with the 1/16-inch ID Teflon tube in place for NaPB injection is shown in Figure 2-4. As indicated in Section 2, three flanges were exposed at ~99ºF. Flanges 1 and 2 were not insulated. Flange 1 was allowed to accumulate borate salts that developed as a result of leakage. Flange 2 was cleaned intermittently. Flange 3 was insulated with NUKON™ and was allowed to accumulate borate salts during the test period.

The orientation of the bolts installed in each flange is shown in Figure 4-3 to Figure 4-5. Upon receipt, bolts were rinsed with acetone, cleaned with RBS-35 solution (a mildly basic surfactant containing anionic and nonionic detergents) in an ultrasonic bath, rinsed with DI water and then air dried. Testing began on September 3, 2013. The temperature during the test was 99.3 ± 2.7°F.

Since mockup tests had indicated that all bolts would be exposed to the NaPB solution at an injection flow rate of 0.5 g/minute, and it was desired to limit the exposure to primarily one bolt, the injection flow rate target was set at 0.1 g/minute. Initially, injection was performed at 0.3 g/min using a peristaltic pump. Flow was then decreased to 0.06 g/min by changing the pump tubing size. On September 5, the bolts were removed from the three flanges, rinsed with acetone to assure the absence of any organic residual and reweighed. Injection was reestablished at 11:10 on the same day at 0.06 ml/minute. A final flow adjustment was made on September 10. Thereafter, the flow rates varied from ~0.08-0.14 g/min through the remainder of the test (Figure 4-6).

Flange 2 was periodically cleaned using a wire brush to remove salts accumulated during testing. Cleanings were performed at 17 days, 27 days and 45 days during the test. Photographs of Flange 2 before and after removing salts at day 27 are shown in Figure 4-7 and Figure 4-8. There was no evidence of the NaPB solution reaching the outside surface of the Flange 3 NUKON™ insulation.

Flow was terminated, and the oven was shut off on October 30 at 16:10 after approximately two months of exposure. The bolts and flanges were allowed to dry overnight. Bolts were removed on October 31. After disassembly of the flanges, bolts were weighed and then soaked in 2.5% NaPB solution to dissolve readily soluble salts, dried, weighed, rinsed with demineralized water, brushed with a soft bristle brush, dried and reweighed.

Initial and final weights of the bolts exposed for approximately two months to the 12% NaPB solution at ~95ºF are given in Figure 4-1. General corrosion rates were estimated from the weight decrease of each specimen. No residual oxide generally appeared present on the specimens following brushing and rinsing. Results can be summarized as follows:

- In Flanges 1 and 2, which were not insulated, the bolts onto which the NaPB solution was injected had significantly greater metal losses than the other bolts in these flanges. Note that the velocity of the solution impinging on the bolt was very low (~0.003 ft/s) so the effect was not a result of erosion-corrosion. It was related to the local solution chemistry that developed on the bolt surface as the water evaporated and the borate salts crystallized.
- In the insulated flange, Bolt 9 onto which the NaPB solution was injected and Bolt 10 which was offset by 90o from the injection location had similar and significantly greater metal losses than the other bolts.
- The weight losses from Bolt 5 in Flange 1, Bolt 1 in Flange 2 and Bolts 9 and 10 in Flange 3 were very similar, i.e., 0.31 to 0.40 grams with an average of 0.36 ± 0.04 grams. This corresponds to an

average metal release rate and corrosion rate of 0.75 ± 0.08 g/dm^2-month based on an estimated area of 0.27 dm^2 for the bolt shank and total threaded length. If the metal loss were limited to the bolt shank and the threaded region above the nut (an estimated area of 0.15 dm^2), the average metal release and corrosion rate would be 1.35 ± 0.14 g/dm^2-month.

- The average observed weight loss of the remaining eight bolts in the three flanges was 0.07 grams. This corresponds to an average metal loss rate of 0.15 ± 0.09 g/dm^2-month based on an estimated area of 0.27 dm^2 for the bolt shank and total threaded length.
- After a year of exposure at an estimated metal loss rate of 0.75 g/dm^2-month, i.e., a weight loss of 9000 mg/dm^2 for the bolt shank and total threaded area, the average metal loss would be ~4.5 mils or 0.0045 inches corresponding to a bolt diameter decrease of ~0.009 inches. If the metal loss were limited to the bolt shank and the threaded region above the nut (an estimated area of 0.15 dm^2), i.e., the NaPB solution did not impact significantly on the corrosion rate in the nut/bolt interface region or in the threaded area of the bolt below the nut, the metal loss would be ~ 8 mils or 0.008 inches corresponding to a bolt diameter decrease of ~0.016 inches after a year of exposure.

Pictures of the bolts before and after removal of deposits are given in Appendix B. Although a rust colored deposit was generally observed on all bolts following removal, there was no visual indication of local corrosion attack on any of the bolts after they were soaked in 2.5% NaPB solution at room temperature to dissolve readily soluble salts, dried, rinsed, brushed with a soft bristle brush, and dried before final reweighing.

4.2 Flange Tests at 203°F

Exposure of Flange 4 at ~203°F began on September 24 at 14:00. The flange was not insulated and was not cleaned during the exposure. The NaPB solution was injected through a 1/16-inch ID Teflon tube onto Bolt 13. The flow rate during the exposure ranged from 0.09 to 0.12 g/min (Figure 4-9). The test temperature was maintained between 199 and 207°F.

The orientation of the bolts in Flange 4 is shown in Figure 4-10. A photograph of the flange after one week of exposure is shown in Figure 4-11. Flow was terminated on November 18 at 09:15 after 8 weeks of exposure. Bolts were removed, dried, and weighed. In an attempt to remove the tightly adherent deposits, bolts were placed in individual sealed bags containing dilute (~2%) NaPB solution and suspended in an ultrasonic bath for 35 minutes. Minimal deposit removal occurred during this process, and bolts were allowed to soak in the dilute NaPB solution overnight. Subsequent inspection indicated that deposits still remained tightly adhered to all four bolts. Using demineralized water as a lubricant, a clean nut was used to chase the threads and remove deposits. Bolts were rinsed with demineralized water and allowed to dry under a heat lamp for one hour.

Pictures of the bolts before and after attempts to remove the deposits by rinsing and chasing the threads are presented in Figure 4-12 to Figure 4-15. As shown, white deposits were still observed between the threads on all four bolts. Bolts were then scrubbed with a wire brush under flowing hot tap water, soaked in demineralized water and placed in an ultrasonic bath for five minutes. This process effectively removed the deposits, and there was no visual indication of residual deposits or metal oxide. The bolts were then dried and reweighed.

Weight losses of individual bolts after exposure for approximately 8 weeks to the 12% NaPB solution at ~200°F are given in Figure 4-2. General corrosion rates were estimated from the weight decrease of each specimen. Only a minimal amount of residual oxide generally appeared present on the specimens following brushing and rinsing. Results can be summarized as follows:

- Bolt 13, onto which the 12% NaPB solution was injected, had a weight loss of 1.038 grams which was significantly greater than that of the other bolts.
- Bolts 14 and 16 (which were offset by 90o from bolt 13) had significant but lower weight losses than Bolt 13, i.e., 0.42 and 0.74 grams, respectively. Bolt 15 which was located 180o from the injection location had significantly less metal loss than the other three bolts (0.07 grams). This suggests that the sodium pentaborate solution was distributing over a greater area of the flange face during these tests than during the 100oF tests. This could be an effect of temperature due to the lower viscosity of the NaPB solution at higher temperature or a slight difference in the leveling of the test flanges.
- The weight losses from Bolts 13, 14 and 16 correspond to average metal loss and corrosion rates of 2.14, 0.85 and 1.51 g/dm^2-mo, respectively, based on an estimated area of 0.27 dm^2 for the bolt shank and total threaded length.
- Over a one year exposure at an estimated weight loss rate of 2.14 g/dm^2-mo, i.e., a weight loss of 25,700 mg/dm^2 for the bolt shaft and total threaded area, the average metal loss would be ~13 mils or 0.013 inches corresponding to a bolt diameter decrease of ~0.026 inches. If the metal loss were limited to the bolt shaft and the threaded region above the nut (an estimated area of 0.15 dm^2), i.e., the NaPB solution did not impact significantly on the corrosion rate in the nut/bolt interface region or in the threaded area of the bolt below the nut, the average metal loss over the remaining length of the bolt would be ~22 mils or 0.022 inches corresponding to a bolt diameter decrease of ~0.044 inches.

Observations of the bolt surfaces viewed at 80x magnification under a microscope after the final cleaning process were as follows:

- Bolt 13 – Limited amounts of crystal deposits were present in the deepest grooves between some threads. There were no visible signs of pitting or other localized corrosion. Some local loss of material due to corrosion was present on the bolt shank (Figure 4-16).
- Bolt 14 – Limited crystal deposits were observed between some threads. Oxidation was observed at the bottom of the threads. Portions of a black outer layer were flaked off the shank of the bolt.
- Bolt 15 – Oxidation was apparent at a few locations, but corrosion appeared minimal.
- Bolt 16 – Limited amounts of white crystals were present in the thread grooves. Some local loss of material due to corrosion was present on the bolt shank (Figure 4-17).

Since there was evidence of localized corrosion in the shank region of Bolts 13 and 16, and the metal loss indicated that there should be a measurable decrease in the shank diameter of these bolts if corrosion was primarily in the shank region and threaded region above the nut, measurements of the shank diameter for all of the flange bolts including three new bolts were made at two locations around the bolt circumference (offset by 90°). Results are given in Table 4-3. As shown, there was a decrease of 0.004 to 0.005 inches in the shank diameter of Bolt 13 at the location of the simulated leak. This bolt had the largest weight loss (1.038 grams) during the test at 203°F. The observed diameter decrease is in reasonable agreement with the values of 0.004 to 0.007 inches estimated from the weight loss data. The diameter decrease for Bolt 16 also is in reasonable agreement with the estimated corrosion rates. No quantifiable decrease in shank diameter was observed for any of the bolts exposed at 95°F which is consistent with the weight loss observations.

Figure 4-1: Bolt Weight Changes after Exposure to Sodium Pentaborate Solution at 95°F
(Solution injected onto Bolts 1, 5 and 9)

	Flange 2[a]				Flange 1[a]				Flange 3[a]			
Bolt	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Initial Weight (9/5/13)	66.4796	66.5065	66.4571	66.4799	66.4673	66.4836	66.4922	66.4302	66.5883	66.4855	66.4823	66.4065
Weight prior to rinse, g	66.2966		66.4837		66.3659	66.8664	66.5480	66.4243	66.4830	66.4265	66.7176	66.4063
Weight post rinse, g	66.1864	66.5020		66.4880	66.0864	66.4819	66.4179	66.3259	66.2383	66.4529	66.7186	66.3155
Weight post brushing, g	66.1686	66.4761	66.4400	66.4332	66.0628	66.4076	66.3863	66.2777	66.2092	66.1266	66.4176	66.3090
Total weight loss, g	**0.311**	**0.030**	**0.017**	**0.047**	**0.404**	**0.076**	**0.106**	**0.153**	**0.379**	**0.359**	**0.065**	**0.097**
Weight loss, g/dm^2-mo[b]	**0.65**	**0.06**	**0.04**	**0.10**	**0.84**	**0.16**	**0.22**	**0.32**	**0.79**	**0.74**	**0.13**	**0.20**

a. Flange 2 intermittently cleaned with a wire brush; Flange 1 allowed to accumulate borate salts over test period; Flange 3 insulated and allowed to accumulate borate slats over test period
b. Based on an area of 0.27 dm^2 for the bolt shank and total threaded length

Figure 4-2: Bolt Weight Changes after Exposure to Sodium Pentaborate Solution at 200°F (Solution injected onto Bolt 13)

	Flange 4			
Bolt	**13**	**14**	**15**	**16**
Initial Weight (9/23/13)	66.4409	66.4609	66.3811	66.4144
Weight prior to soak, g	67.7621	67.6227	66.7076	67.7891
Weight after 1st deposit removal, g	65.5036	66.1667	66.3352	65.9212
Weight after 2nd deposit removal, g	65.4029	66.0460	66.3141	65.6785
Total weight loss, g	**1.038**	**0.415**	**0.067**	**0.736**
Weight loss, g/dm^2-mo[a]	**2.14**	**0.85**	**0.14**	**1.51**

a. Based on an area of 0.27 dm^2 for the bolt shank and total threaded length

Figure 4-3: Flange #1 Bolt Configuration as Viewed from Top of Flange (Arrow indicates injection location)

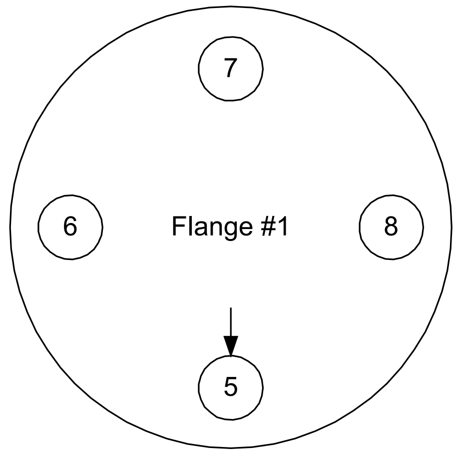


Figure 4-4: Flange #2 Bolt Configuration as Viewed from Top of Flange (Arrow indicates injection location)

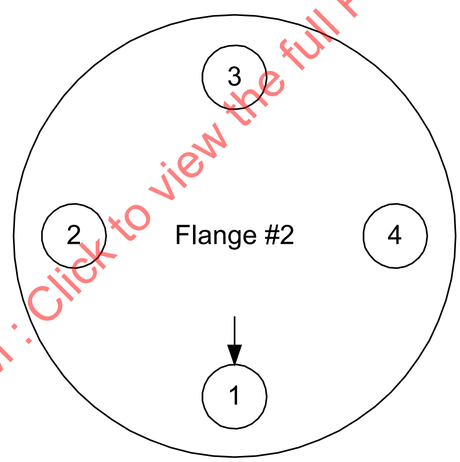


Figure 4-5: Flange #3 Bolt Configuration as Viewed from Top of Flange (Arrow indicates injection location)

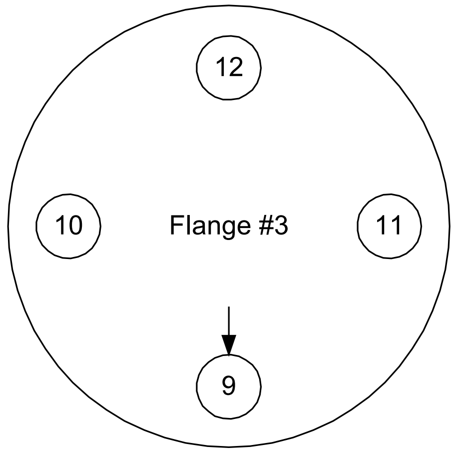


Figure 4-6: Low Temperature Flange Injection Flow Rates

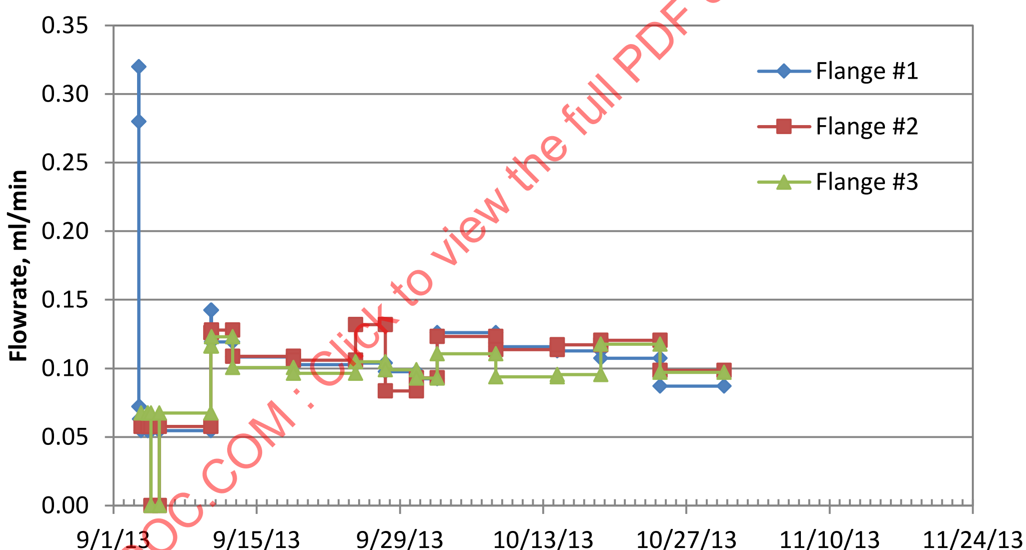


Figure 4-7: Flange #2 Prior to Removing Salts after 27 Days of Exposure

Figure 4-8: Flange #2 after Removing Salts after 27 Days of Exposure

Figure 4-9: Flange # 4 Injection Flow Rate

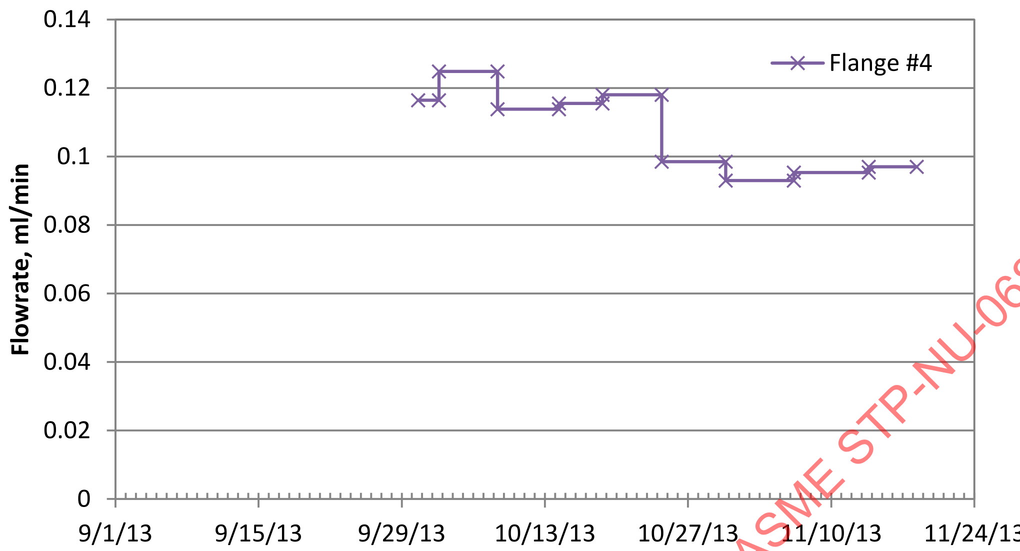


Figure 4-10: Flange #4 Bolt Configuration as Viewed from Top of Flange

(Arrow indicates injection location)

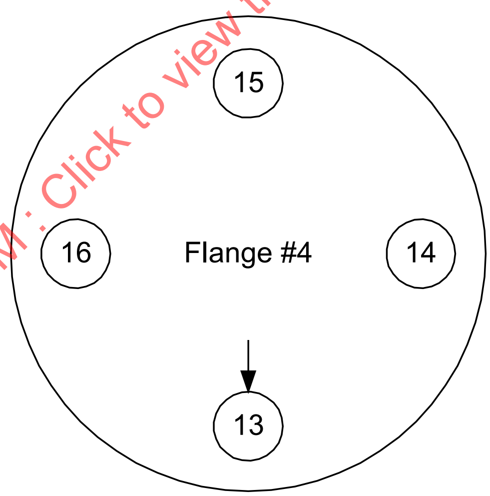


Figure 4-11: Flange #4 after One Week Exposure at 200°F

Figure 4-12: Bolt 13 before and after Initial Deposit Removal

Bolt 13 before removal (0°)

Bolt 13 before removal (180°)

Bolt 13 after initial deposit removal (0°)

Bolt 13 after initial deposit removal (180°)

Figure 4-13: Bolt 14 before and after Initial Deposit Removal

Bolt 14 before removal (0°)

Bolt 14 before removal (180°)

Bolt 14 after initial deposit removal (0°)

Bolt 14 after initial deposit removal (180°)

Figure 4-14: Bolt 15 before and after Initial Deposit Removal

Bolt 15 before removal (0°)

Bolt 15 before removal (180°)

Bolt 15 after initial deposit removal (0°)

Bolt 15 after initial deposit removal (180°)

Figure 4-15: Bolt 16 before and after Initial Deposit Removal

Bolt 16 before removal (0°)

Bolt 16 before removal (180°)

Bolt 16 after initial deposit removal (0°)

Bolt 16 after initial deposit removal (180°)

Figure 4-16: Bolt 13 after Final Cleaning

Figure 4-17: Bolt 16 after Final Cleaning

Figure 4-18: Measurements of Bolt Shank Diameter

		Average	
Bolt No.	Test Temp, °F	0° & 180°	90° & 270°
1	95	0.497	0.497
2	95	0.498	0.497
3	95	0.498	0.498
4	95	0.497	0.498
5	95	0.497	0.496
6	95	0.498	0.497
7	95	0.497	0.497
8	95	0.496	0.496
9	95	0.498	0.497
10	95	0.497	0.498
11	95	0.497	0.498
12	95	0.498	0.498
13	200	0.492	0.493
14	200	0.497	0.496
15	200	0.497	0.497
16	200	0.492	0.494
Blank 1	N/A	0.496	0.498
Blank 2	N/A	0.497	0.498
Blank 3	N/A	0.496	0.497

5 SUMMARY

Corrosion of A193 Grade B7 bolting used in stainless steel flanges installed in BWR sodium pentaborate (NaPB) systems was evaluated during a series of laboratory tests. In the first series of tests, coupons of selected materials including Alloy C4140, the base material for the A193 Grade B7 bolt material, were exposed at ~95ºF and 185ºF to 12% sodium pentaborate solutions over periods of one to two months. Corrosion of all tested materials was minimal. Results from the 95°F coupon test yielded weight loss rates of <5 mg/dm^2-month after two months of exposure, with many of the coupons showing increases in weight. Results from the coupon tests at 185°F yielded similar results with weight losses of <2 mg/dm^2-month after two months of exposure.

It should be noted that bolts manufactured from the C4140 material must be heat treated to meet ASTM A193 B7 specifications. A typical processing entails treatment at ~1550ºF for 30 to 60 minutes, quenching, and then tempering at a minimum of 1100ºF for ~60 minutes. This leads to formation of an oxide film on the surface of the bolts. As a result, corrosion characteristics of the untreated C4140 coupons and the bolts could differ significantly.

In a second series of tests, A193 Grade B7 bolts were submerged in 12% NaPB and in demineralized water at 95°F. The bolt submerged in the NaPB solution showed no loss of weight after a two month exposure, and the NaPB solution remained clear. The bolt exposed to air saturated demineralized water exhibited a weight loss of approximately 180 mg/dm^2-month or approximately 1 mil per year. Significant oxidation of the bolt exposed to demineralized water was apparent after approximately 24 hours, and the solution became rust colored.

A third series of tests with 4" diameter stainless steel flanges with four A193 Grade B7 bolts was also performed. Leakage through the flange gasket was simulated by continuously injecting a 12% NaPB solution onto one of the bolts through a 1/16-inch diameter Teflon tube. Three flanges were exposed at ~99ºF. Two flanges were not insulated. Flange 1 was allowed to accumulate borate salts that developed as a result of leakage. Flange 2 was cleaned intermittently. Flange 3 was insulated with NUKON™ and was allowed to accumulate borate salts during the test period. A test also was performed with an uninsulated flange exposed at ~203ºF. Deposits formed during the two month exposure were allowed to accumulate on the flange.

At both 99 and 203ºF, the bolt onto which the NaPB solution was injected exhibited the highest weight loss. The maximum weight losses in the three configurations tested at 99ºF varied from 0.65 to 0.84 g/dm^2-month based on an estimated corrosion area of 0.27 dm^2 for the bolt shank and total threaded length. At the maximum weight loss of 0.84 g/dm^2-month, the weight loss over 1 year would be 10.1 g/dm^2 which corresponds to a metal loss of approximately 5.0 mils and a bolt diameter decrease of ~10 mils/year. The maximum weight loss during the 203°F tests was 2.14 g/dm^2-month which corresponds to a metal loss of approximately 26 g/dm^2 or 13 mils per year and a bolt diameter decrease of ~26 mils/year.

6 REFERENCES

[1] Boric Acid Corrosion of Carbon and Low Alloy Steel Pressure boundary Components In PWRs, EPRI, Palo Alto CA: August 1988. NP-5985

[2] A Survey of the Literature on Low Alloy Steel Fastener Corrosion in PWR Power Plants. EPRI, Palo Alto CA: December 1984. NP-3784

[3] Metal Samples Company, Munford, AL, May 2013

APPENDIX A: Certificates of Compliance

McMASTER-CARR®

Purchase Order
10190

Page 1 of 1

9630 Norwalk Boulevard
Santa Fe Springs, CA 90670-2932
630-600-3600
la.sales@mcmaster.com

N W T CORP
7015 REALM DR
SAN JOSE CA 95119-1321
ATTENTION: MATT LEONARD

McMaster-Carr Number
1605662-01

04/09/13

Line		Description	Ordered	Shipped
1	**94705A209**	GRADE B7 ALLOY STEEL HEAVY HEX HEAD BOLT 1/2"-13 THREAD, 2" LENGTH	**12 Each**	**12**
2	**44685K33**	LOW-PRESSURE 304/304L STAINLESS STEEL FLANGE SLIP ON, 1 PIPE SIZE, 4-1/4" OD	**6 Each**	**6**
3	**94485A033**	ASTM A194 GRADE 7 ALLOY STEEL HEAVY HEX NUT 1/2"-13 THREAD SIZE, 7/8" WIDTH, 31/64" HEIGHT	**2 Pack**	**2**

Certificate of compliance

This is to certify that the above items were supplied in accordance with the description and as illustrated in the catalog. In all other respects this transaction remains subject to our standard terms and conditions of sale, which can be found at www.mcmaster.com.

Gabriel Priyev

Gabriel Priyev, Compliance Manager

McMASTER-CARR

9630 Norwalk Blvd
Santa Fe Springs CA 90670-2932
562-692-5911
ales@mcmaster.com

N W T Corp
7015 Realm Dr
San Jose CA 95119-1321

Purchase Order
10229

Page 1 of 1

Order Placed By
Matt

07/16/2013

McMaster-Carr Number
5472796-01

LNS AA

Line		Description	Ordered	Shipped		
1	**94705A209**	Grade B7 Alloy Steel Heavy Hex Head Bolt, 1/2"-13 Thread, 2" Length	10 Each	10	3 - 629 - 03 04 - 98 A209 10 EA	1
2	**44685K33**	Low-Pressure 304/304L Stainless Steel Flange, Slip on, 1 Pipe Size, 4-1/4" OD	2 Each	2	2 - 432	2

Certificate of compliance

This is to certify that the above items were supplied in accordance with the description and as illustrated in the catalog. In all other respects this transaction remains subject to our standard terms and conditions of sale, which can be found at www.mcmaster.com.

Kirk McGettigan
Compliance Manager

N W T Corp

A
3X6X5 A

6 lbs
2 lines

SW1BFP36
07/16/2013
15:54/16:03
434
Cycle 85

APPENDIX B: Low Temperature Test Photographs

Bolt 1 before removal (0°)

Bolt 1 before removal (180°)

Bolt 1 after deposit removal (0°)

Bolt 1 after deposit removal (180°)

Bolt 2 before removal (0°)

Bolt 2 before removal (180°)

Bolt 2 after deposit removal (0°)

Bolt 2 after deposit removal (180°)

Bolt 3 before removal (0°)

Bolt 3 before removal (180°)

Bolt 3 after deposit removal (0°)

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