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Corrosion Studies on GeoBrom® HG520

Total Immersion Study

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brominated derivative products for mercury control

Contents

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Background Information

A 90-day, total-immersion corrosion rate study was conducted using GeoBrom® HG520 calcium bromide solution and six selected metals at 20° and 50° C. ASTM Method "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens" G1 - 03 (reapproved 2011) was used to prepare, clean, and evaluate tests specimens.

The following six metals were evaluated:

- **C-1018** mild carbon steel coupon
- **304-W** 304SS welded coupon
- **316-LW** 316SS, low carbon, welded coupon
- **2205** Duplex 2205 coupon
- **304-LW** 304SS, low carbon, welded coupon
- **316** 316SS coupon

Objectives of the Study

1. Establish subsurface corrosion rates at 20° C and 50° C for each metal.
2. Visually document coupon condition before and after 90 day exposure.
3. Analyze solution for metal content before and after 90 day exposure to evaluate metals in test solution.

Executive Summary

All specimens were less than 2.0 mpy corrosion rate based on this 90 day total-immersion study. Mild carbon steel (C-1018) had the highest rates at 0.32 mpy at 20° C and 1.29 mpy at 50° C. All remaining specimens were under 0.05 mpy. ICP analysis indicated elevated iron content in test solutions at the end of the 90 day period. General surface corrosion was observed on both C1018 coupons with some pitting at 50° C. There was no visible corrosion on remaining test specimens. The maximum allowable corrosion rate for each specimen with GeoBrom® HG520 depends on the application.

Description of Test Procedure

Metal test coupons with dimensions of ~ 2.0" x 0.75" x 0.125" were supplied by an outside vendor. The vendor prepared the coupons by abrading surfaces and stamping metal type and marking specimens with a unique identification number. Prior to using, coupons were cleaned using reagent grade aqueous HCl and a bristle brush followed by a thorough deionized water rinse, degreased using acetone, dried using hot air, then allowed to cool in desiccators. The clean, dry specimens were weighed and measured. Using forceps, a four place OHAUS Galaxy Model G160D analytical balance was used to attain initial weights for all coupons. Dimensions were established using a Starrett® Micrometer part # 436RL-1, EDP 51568 and a Starrett® Dial Caliper Part # 120Z, EDP 55951. Three measurements were taken on all dimensions and averaged for the length, width, and thickness. Pictures were taken to record coupon condition prior to beginning immersion tests.

Test coupons were split into two groups containing specimens of each metal type, and placed into two glass one-liter bottles with Teflon® liners. One group was placed in a Yamato Model DVS600 drying oven to hold samples at 50° C, and the second group was placed in a controlled environment room held at 20° C. There was no agitation or aeration of the test specimens while in the glass bottles.

Duration of the test was 90 days or 2,160 hours. Prior to cleaning, pictures were taken to record coupon condition after the 90 day immersion test. After cleaning, pictures were taken again. None of the specimens were heavily corroded, so post immersion cleaning was simple and consisted of the following:

1. Immersion in deionized water to remove test solution
2. Immersion and brushed in aq. HCl (for mild carbon steel), and nitric acid (for the stainless steels)
3. Thoroughly rinsed with deionized water, then immediately dried.

The C1018 coupon required scrubbing with a mild abrasive in deionized water. Table A1.1 in ASTM G1-03 was used as a guide to select cleaning procedure for removal of corrosion products. After drying test specimens with hot air and then allowing them to cool in desiccators, all specimens were re-weighed and the final weights recorded.

Spreadsheets were developed to capture data and to make calculations per ASTM method. Calculated metal densities and published metal densities were used in corrosion rate calculations for comparison.

The average corrosion rate calculation per ASTM G1-03 is:

Corrosion Rate = (K x W) / (A x T x D)

- **K** = a constant "(K) constant listed in ASTM G1-03, Section 8 for desired units"
- **T** = time of exposure in hours
- **A** = area in cm2
- **W** = mass loss in grams
- **D** = density in gm/cm3

Results and Discussion

Tables 1 and 2 provide data on test specimens at 20° C and at 50° C, respectively. Corrosion rates on all specimens were under 2.0 mpy rate. Mild carbon steel C-1018 gave the highest corrosion rate at 0.32 mpy at 20° C and 1.29 mpy at 50° C. General surface corrosion was observed on C-1018 coupons with some pitting on the C-1018 coupon at 50° C. There was no surface corrosion or pitting observed visually on any remaining specimens.

Corrosion rates for each specimen were charted to reflect trends over the two temperatures 20° C and 50° C **(see Figures 1-2)**.

GeoBrom® HG520 test solutions were also submitted for inductively coupled plasma (ICP) analysis before and after the immersion test. ICP data contained in **Table 3** provides metals concentrations in test fluids at start, at end, and the difference between the two. There is a significant increase in iron (Fe) concentrations in the post-test solutions from the corrosion of the carbon steel coupons.

To visually document condition of test specimens, pictures were taken before immersion tests, after, then after cleaning **(see Figures 3-10)**.

Table 4 shows the chemical composition of each test specimen.

Conclusion

C-1018 showed signs of corrosion in this test. There are a number of different corrosion standards depending on the application. Therefore, whether C-1018 is suitable for use with $CaBr_2$ depends on the application. These data are relevant only to the 52% $CaBr_2$ solution. Dilute solutions or other uses of 52% solution may exhibit different corrosive behaviors.

Table 1

Subsurface at 20° C

Corrosion Coupon Testing with GeoBrom® HG520 Solution → Below Surface at 20° C

May 31, 2013 - August 29, 2013

Total Exposure Time: 90 Days

Using ASTM Designation: G1 - 03 (reapproved 2011) standard practice for preparing, cleaning, and evaluating corrosion test specimens

Coupon Type	C-1018	304-W	316-LW	Duplex 2205	304-LW	316
Identification Mark	A1686	A0023	A8151	single dot	A0012	A1170
Weight (grams)	22.1947	22.8463	20.0253	21.9995	22.9181	19.7559
Length (inches)	2.017	2.003	2.003	2.017	2.008	1.989
Width (inches)	0.771	0.756	0.746	0.763	0.759	0.750
Thickness (inches)	0.123	0.129	0.115	0.123	0.130	0.112
Hole dia. (inches)	0.376	0.375	0.377	0.377	0.375	0.380
Calculated Density (gm/cc)	7.627	7.674	7.719	7.674	7.641	7.792
Published Density (gm/cc) ASTM	7.86	7.94	7.94	7.805	7.94	7.98
Calculated Surface Area (sq. cm)	23.991	23.714	22.776	23.757	23.844	22.607
Start date (MDY)	5/31/2013	5/31/2013	5/31/2013	5/31/2013	5/31/2013	5/31/2013
Start time (hours)	14:35	14:35	14:35	14:35	14:35	14:35
End date (MDY)	8/29/2013	8/29/2013	5/31/2013	5/31/2013	5/31/2013	8/29/2013
End time (hours)	14:35	14:35	14:35	14:35	14:35	14:35
Temperature (°C)	20	20	20	20	20	20
Exposure Time (hours)	2,160	2,160	2,160	2,160	2,160	2,160
Ending Weight (grams)	22.1585	22.8455	20.0233	21.9992	22.9161	19.7551
Loss in Weight (grams)	0.0362	0.0008	0.002	0.0003	0.002	0.0008
Rate of Corrosion (mpy) using calculated density	0.3160	0.0070	0.0182	0.0026	0.0175	0.0073
Rate of Corrosion (mpy) using published density	0.3066	0.0068	0.0177	0.0026	0.0169	0.0071

Observations :

1. Mild carbon steel shows the highest corrosion rate at 0.316 mpy at 20° C based on a 90-day exposure time.
2. Coupons of 304-W, 316-LW, Duplex 2205, 304-LW, and 316 were all below 0.05 mpy.

Table 2

Subsurface at 50° C

Corrosion Coupon Testing with GeoBrom® HG520 Solution → Below Surface at 50° C

May 31, 2013 - August 29, 2013

Total Exposure Time: 90 Days

Using ASTM Designation: G1 - 03 (reapproved 2011) standard practice for preparing, cleaning, and evaluating corrosion test specimens

Coupon Type	C-1018	304-W	316-LW	Duplex 2205	304-LW	316
Identification Mark	A1685	A0024	A8153	double dot	A0013	A1169
Weight (grams)	22.3493	23.0076	20.17	21.9338	22.7433	19.9863
Length (inches)	2.018	2.005	2.000	2.017	2.006	2.001
Width (inches)	0.773	0.760	0.749	0.762	0.758	0.750
Thickness (inches)	0.124	0.130	0.115	0.122	0.129	0.113
Hole dia. (inches)	0.375	0.373	0.377	0.378	0.375	0.380
Calculated Density (gm/cc)	7.574	7.637	7.694	7.697	7.657	7.757
Published Density (gm/cc) ASTM	7.86	7.94	7.94	7.805	7.94	7.98
Calculated Surface Area (sq. cm)	24.127	23.867	22.870	23.702	23.760	22.797
Start date (MDY)	5/31/2013	5/31/2013	5/31/2013	5/31/2013	5/31/2013	5/31/2013
Start time (hours)	14:35	14:35	14:35	14:35	14:35	14:35
End date (MDY)	8/29/2013	8/29/2013	8/29/2013	8/29/2013	8/29/2013	8/29/2013
End time (hours)	14:35	14:35	14:35	14:35	14:35	14:35
Temperature (°C)	50	50	50	50	50	50
Exposure Time (hours)	2,160	2,160	2,160	2,160	2,160	2,160
Ending Weight (grams)	22.2015	23.0066	20.1696	21.9322	22.7382	19.9855
Loss in Weight (grams)	0.1478	0.001	0.0004	0.0016	0.0051	0.0008
Rate of Corrosion (mpy) using calculated density	1.2918	0.0088	0.0036	0.0140	0.0448	0.0072
Rate of Corrosion (mpy) using published density	1.2448	0.0084	0.0035	0.0138	0.0432	0.0070

Observations :

1. Mild Carbon steel shows the highest corrosion rate at 1.2918 mpy at 50° C based on a 90-day exposure time.
2. Coupons of 304-W, 316-LW, Duplex 2205, 304-LW, and 316 were all below 0.05 mpy.

Table 3

Metals in Test Fluid

ICP Analysis Before and After 90-Day Total-Immersion Corrosion Rate Study

All results in mg/L

		ref ICP spl #1	ref ICP spl #3		ref ICP spl #2	ref ICP spl #4	
		Metals in sample	Metals in sample	20° C Test	Metals in sample	Metals in sample	50° C Test
Metal ID		B-04 before	B-04 after at 20° C.	Difference	B-05 before	B-05 after at 50° C	Difference
Ag	(Silver)	4.23	4.85	0.62	4.26	4.81	0.55
Al	(Aluminum)	3.78	4.75	0.97	3.89	4.42	0.53
As	(Arsenic)	8.77	0.00	-8.77	3.55	5.12	1.57
B	(Boron)	0.92	1.05	0.13	1.04	1.11	0.07
Ba	(Barium)	5.72	5.88	0.16	5.78	5.93	0.15
Be	(Beryllium)	0.00	0.00	0.00	0.00	0.00	0.00
Bi	(Bismuth)	10.97	9.97	-1.00	11.97	11.83	-0.14
Ca	(Calcium)	very high	very high	N/A	very high	very high	N/A
Cd	(Cadmium)	1.14	2.24	1.10	1.70	2.93	1.23
Ce	(Cerium)	13.64	15.37	1.73	16.25	15.56	-0.69
Co	(Cobalt)	3.25	3.12	-0.13	3.41	3.17	-0.24
Cr(II)	(Chromium)	6.69	5.17	-1.52	5.78	8.86	3.08
Cu	(Copper)	1.50	1.45	-0.05	1.40	1.54	0.14
Fe(II)	(Iron)	3.25	53.95	50.70	6.39	139.86	133.47
K	(Potassium)	168.11	166.39	-1.72	149.46	184.31	34.85
La	(Lanthanum)	61.13	61.93	0.80	66.21	62.88	-3.33
Li	(Lithium)	6.15	6.41	0.26	6.48	6.29	-0.19
Mn	(Manganese)	3.51	4.47	0.96	3.58	7.00	3.42
Mo	(Molybdenum)	11.03	11.99	0.96	9.44	10.15	0.71
Na	(Sodium)	3.36	3.49	0.13	3.34	3.75	0.41
Ni	(Nickel)	3.55	2.40	-1.15	3.29	2.71	-0.58
Pb	(Lead)	4.22	4.83	0.61	6.30	12.99	6.69
Rb	(Rubidium)	4.74	4.32	-0.42	4.74	5.09	0.35
Sb	(Antimony)	5.27	4.63	-0.64	3.28	7.96	4.68
Se	(Selenium)	uncal	uncal	N/A	uncal	uncal	N/A
Sn	(Tin)	6.57	6.48	-0.09	6.66	10.79	4.13
Sr	(Strontium)	52.08	61.19	9.11	52.39	68.60	16.21
Ti	(Titanium)	2.93	3.03	0.10	2.90	3.03	0.13
Tl	(Thallium)	uncal	uncal	N/A	uncal	uncal	N/A
U	(Uranium)	48.57	29.68	-18.89	43.04	38.00	-5.04
V	(Vanadium)	18.32	21.79	3.47	21.39	29.99	8.60
Zn(I)	(Zinc)	0.00	0.46	0.46	0.00	3.98	3.98

Note: Metals highlighted in the table are major components in the coupons evaluated. Significant increases in the concentration of these metals would be an indication of corrosion of the coupons

Figure 1

Corrosion Rate Trend Chart (with Y Axis at 0 to 1.4 mpy scale)

Corrosion Coupons at 20° and 50° C Subsurface in GeoBrom® HG520 Calcium Bromide Solution

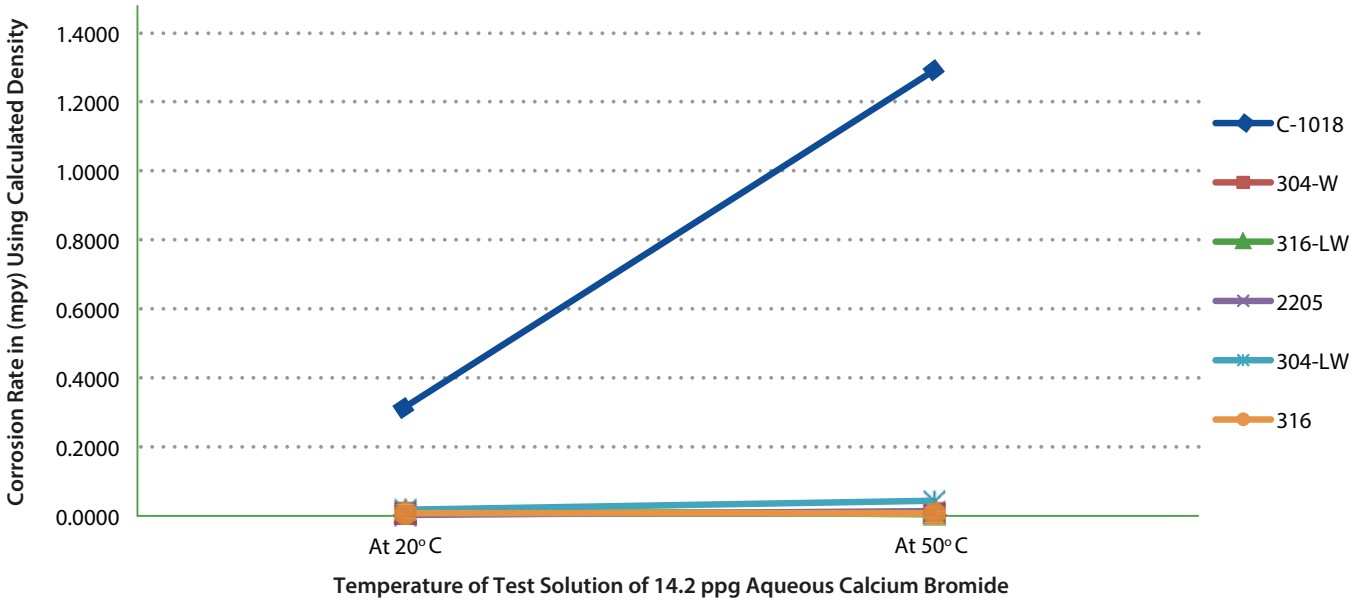

Figure 2

Corrosion Rate Trend Chart (with Y Axis at 0 to 0.07 mpy scale)

Corrosion Coupons at 20° and 50° C Subsurface in GeoBrom® HG520 Calcium Bromide Solution

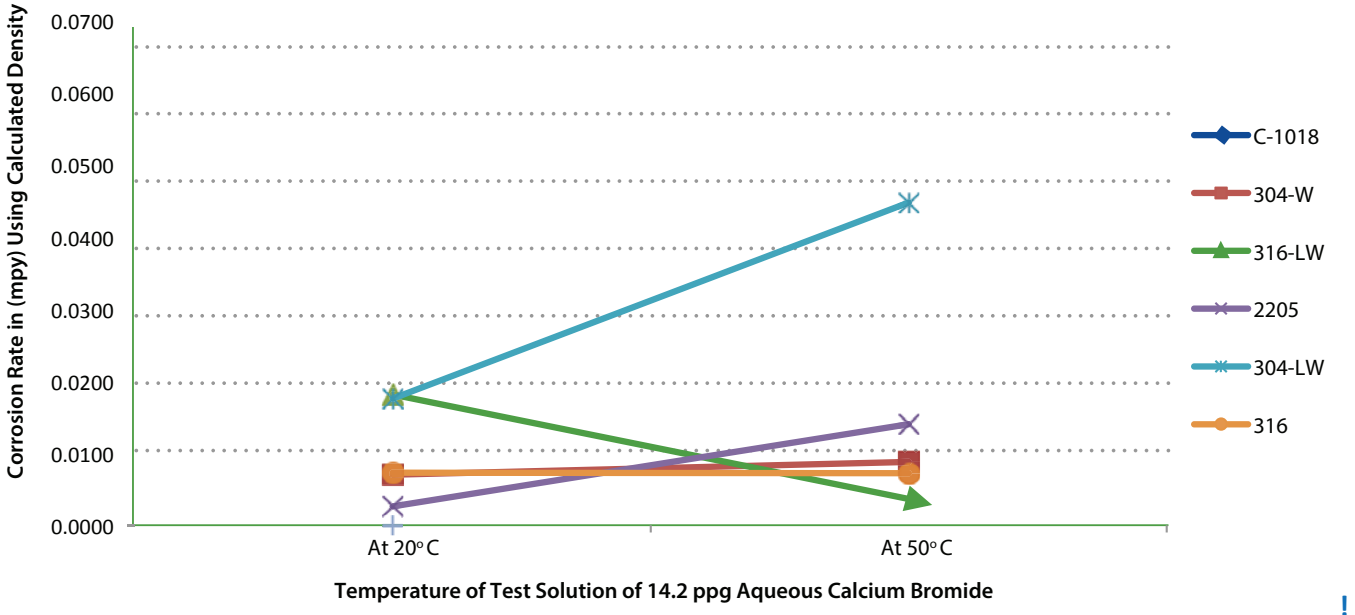

Figure 3

Test Coupons Before 90-Day Subsurface Exposure

Length	WIdth	Thickness	Hole Dime	Grams to Weight		
2.015″ 2.020″ 2.015″	0.771″ 0.771″ 0.771″	0.123″ 0.124″ 0.122″	0.376″	22.1947gm		C1018
2.017″ 2.020″ 2.017″	0.7735″ 0.774″ 0.773″	0.125″ 0.124″ 0.1235″	0.375″	22.3493 gm		C1018
2.017″ 2.018″ 2.016″	0.763″ 0.765″ 0.762″	0.1225″ 0.1225″ 0.1225″	0.377″	21.9995 gm		Duplex 2205
2.017″ 2.017″ 2.017″	0.762″ 0.764″ 0.761″	0.122″ 0.122″ 0.122″	0.378″	21.9338 gm		Duplex 2205
2.004″ 2.004″ 2.002″	0.753″ 0.757″ 0.759″	0.129″ 0.130″ 0.129″	0.375″	22.8463 gm		304W
2.005″ 2.007″ 2.004″	0.758″ 0.760″ 0.761″	0.130″ 0.129″ 0.131″	0.373″	23.0076 gm		304 W

Figure 4

Test Coupons Before 90-Day Subsurface Exposure

Length	WIdth	Thickness	Hole Dime	Grams to Weight		
2.006″ 2.010″ 2.007″	0.757″ 0.760″ 0.760″	0.1305″ 0.129″ 0.1295″	0.375″	22.9181gm		304LW
2.003″ 2.007″ 2.007″	0.757″ 0.758″ 0.760″	0.127″ 0.127″ 0.1275″	0.375″	22.7433 gm		304LW
1.990″ 1.989″ 1.987″	0.749″ 0.754″ 0.752″	0.112″ 0.112″ 0.113″	0.380″	19.7559 gm		316
2.001″ 2.000″ 2.002″	0.750″ 0.752″ 0.748″	0.113″ 0.114″ 0.113″	0.380″	19.9863 gm		316
2.000″ 2.004″ 2005″	0.746″ 0.747″ 0.745″	0.115″ 0.1135″ 0.115″	0.377″	20.0253 gm		316LW
1.997″ 2.003″ 2.000″	0.750″ 0.750″ 0.748″	0.115″ 0.115″ 0.116″	0.377″	20.1700 gm		316LW

Figure 5

Test Coupons After 90-Day Subsurface Exposure at 20° C (before cleaning)

Subsurface at 20° C out 8-29-13 at 14:45
Not cleaned

C 1018
A1686

304 LW
A0012

Duplex
2205
single dot

316
A1170

304
A0023

316 LW
A8151

Figure 6

Test Coupons After 90-Day Subsurface Exposure at 50° C (before cleaning)

Subsurface at 50° C out 8-29-13 at 14:45
Not cleaned

C 1018
A1685

304 LW
A0013

Duplex
2205
two dot

316
A1169

304
A0024

316 LW
A8153

Figure 7

Front Side of C1018 Coupon After 90-Day Subsurface Exposure at 50° C (before cleaning)

C 1018
A1685

Figure 8

Back Side of C1018 Coupon After 90-Day Subsurface Exposure at 50° C (before cleaning)

C 1018
A1685

Figure 9

Test Coupons After 90-Day Subsurface Exposure at 20° C (after cleaning)

Subsurface at 20° C out 8-29-13 at 14:45

C 1018
A1686

304 LW
A0012

Duplex
2205
single dot

316
A1170

304
A0023

316 LW
A8151

Figure 10

Test Coupons After 90-Day Subsurface Exposure at 50° C (before cleaning)

Subsurface at 50° C out 8-29-13 at 14:45
After Cleaning

C 1018
A1685

304 LW
A0013

Duplex
2205
two dot

316
A1169

304
A0024

316 LW
A8153

Table 4

Composition of Specimens

Chemical Composition of Specimens Tested during 90-Day Total Immersion Study

AISI = American Iron and Steel Institute Data in % by weight

Metal Type	AISI 1018	AISI 304	AISI 304-L	AISI 316	AISI 316-L	Duplex 2205
Carbon	0.15 - 0.20	0.08 max	0.03 max	0.08 max	0.03 max	<0.03
Manganese	0.60 - 0.90	2 max	2 max	2 max	3 max	< 2
Phosphorous	0.040 max	0.045 max	0.045 max	0.045 max	0.045 max	< 0.03
Sulfur	0.050 max	0.03 max	0.03 max	0.03 max	0.03 max	< 0.02
Silicon	0.15 to 0.30	0.75 max	0.75 max	1 max	2 max	< 1
Chromium	N/A	18 - 20	18-20	16 - 18	17 - 18	21 - 23
Nickel	N/A	8 to 12	8 to 12	10 to 14	11 to 14	4.5 - 6.5
Molybdenum	N/A	N/A	N/A	2 to 3	2 to 3	2.5 - 3.5
Nitrogen	N/A	0.10 max	0.10 max	N/A	N/A	0.8 - 2.0
Iron	balance	balance	balance	balance	balance	balance

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