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Vapor space study

Corrosion studies on GeoBrom® HG520

X GeoBrom® HG520

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BROMINATED DERIVATIVE PRODUCTS FOR MERCURY CONTROL

Contents

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Background information

A 90-day vapor space 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

- Establish subsurface corrosion rates at 20°C and 50°C for each metal.
- Visually document coupon condition before and after 90 day exposure.

All specimens were less than 0.06 mpy corrosion rate based on this 90-day study. Mild carbon steel (C-1018) gave the highest rates at 0.025 mpy at 20°C and 0.053 mpy at 50°C. All remaining specimens were under 0.015 mpy. Minor surface corrosion was observed on both C1018 coupons. There was no visible corrosion on remaining test specimens, and all test solutions remained water clear after 90 days. 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 vapor exposure tests.

Test coupons were split into two groups, containing specimens of each metal type, and placed into individual 4-oz bottles with Teflon® liners. Coupons were suspended 3/8 inches above the liquid surface using Teflon® string. One group was placed in a Yamato Model DVS600 drying oven to hold samples at 50ºC and the second group placed in a controlled environment room held at 20ºC. There was no agitation or aeration of the test specimens while in the glass bottles.

Duration of the test was 90 days and 1 hour or 2,161 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:

- Immersion in deionized water to remove test solution
- Immersion and brushed in aq. HCl (for mild carbon steel), and nitric acid (for the stainless steels)
- Thoroughly rinsed with deionized water, then immediately dried. The C1018 coupon required light scrubbing using a brush 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 cm^2
- W = mass loss in grams
- D = density in gm/cm^3

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 0.10 mpy rate. Mild carbon steel C-1018 gave the highest corrosion rate at 0.025 mpy at 20 °C and 0.053 mpy at 50 °C. Minor surface corrosion but no pitting was observed on C-1018 coupons. There was no surface corrosion or pitting observed on any remaining specimens suspended above the liquid by ~ 3/8 inches. C-1018 corrosion is likely due to humidity in headspace of bottle.

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

GeoBrom® HG520 test solutions were saved for Inductively Coupled Plasma (ICP) analysis before and after the immersion tests. After the 90-day period, all GeoBrom® HG520 solutions remained water clear. To verify that there was no significant increase in any metals after 90 days, ICP analysis was conducted only on GeoBrom® HG520 used for the C-1018 coupon, since the C-1018 coupon had the highest corrosion rate after 90 days at 50 °C. See Table 4 for metals concentrations in test fluid at start, at end, and the difference. Data verified that there is little to no increase in metals. All bottles were sealed, but a small amount of water vapor may have vented over 90 days resulting in a slight increase in metals.

To visually document condition of test specimens, pictures were taken before and after immersion tests (see Figures 2 – 6).

Conclusion

C-1018 showed signs of a slight surface corrosion in this test and a low corrosion rate. 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.

Figure 1: Corrosion rate trend chart with Y axis at 0 to 0.06 mpy scale

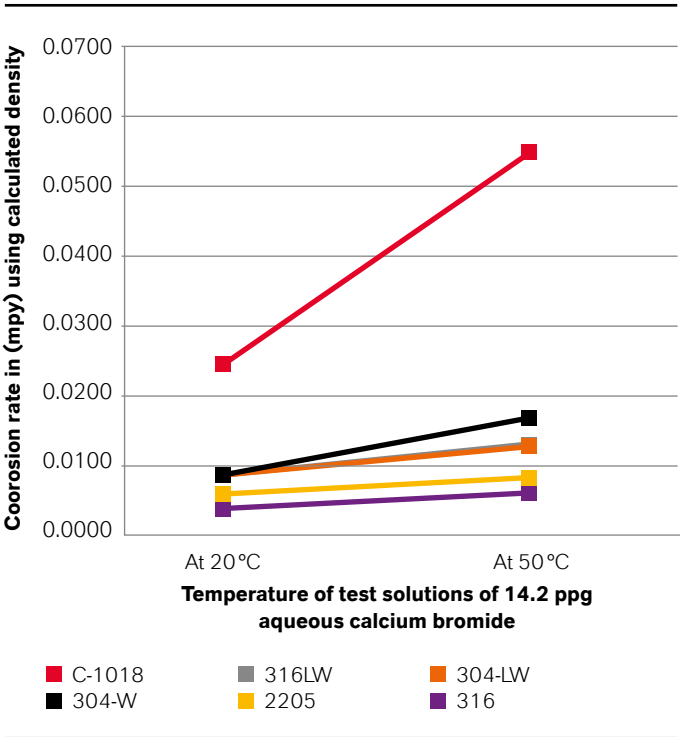


Table 1: Vapor space at 20 °C

Corrosion coupon testing with GeoBrom® HG520 calcium bromide solution – vapor space 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 Identification mark	C-1018 A1689	304-W A0027	316-LW A8156	Duplex 2205 five dot	304-LW A0016	316 A1167
Weight (grams)	22.0307	23.0696	19.9073	21.7531	23.2976	20.1366
Length (inches)	2.016	2.001	2.001	2.015	2.010	1.997
Width (inches)	0.772	0.765	0.746	0.762	0.761	0.750
Thickness (inches)	0.122	0.131	0.114	0.122	0.132	0.114
Hole dia. (inches)	0.375	0.376	0.375	0.377	0.376	0.377
Calculated density (gm/cc)	7.603	7.594	7.685	7.642	7.620	7.762
Published density (gm/cc) ASTM	7.86	7.94	7.94	7.805	7.94	7.98
Calculated surface area (sq. cm)	23.982	23.965	22.763	23.675	24.012	22.812
Start date (MDY)	8/14/2013	8/14/2013	8/14/2013	8/14/2013	8/14/2013	8/14/2013
Start time (hours)	9:30	9:30	9:30	9:30	9:30	9:30
End date (MDY)	11/12/2013	11/12/2013	11/12/2013	11/12/2013	11/12/2013	11/12/2013
End time (hours)	10:30	10:30	10:30	10:30	10:30	10:30
Temperature (°C)	20	20	20	20	20	20
Exposure time (hours)	2161	2161	2161	2161	2161	2161
Ending weight (grams)	22.0278	23.0686	19.9069	21.7526	23.2966	20.1363
Loss in weight (grams)	0.0029	0.001	0.0004	0.0005	0.001	0.0003
Rate of corrosion (mpy) using calculated density	0.0254	0.0088	0.0037	0.0044	0.0087	0.0027
Rate of corrosion (mpy) using published density	0.0246	0.0084	0.0035	0.0043	0.0084	0.0026

Table 2: Vapor space at 50 °C

Corrosion coupon testing with GeoBrom® HG520 solution – vapor space 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	six dot	A0013	A1169
Weight (grams)	21.8898	21.7960	20.0162	21.3550	22.7820	20.0809
Length (inches)	2.018	2.001	2.001	1.999	2.003	2.005
Width (inches)	0.773	0.759	0.749	0.751	0.758	0.750
Thickness (inches)	0.122	0.125	0.114	0.122	0.130	0.114
Hole dia. (inches)	0.378	0.374	0.375	0.382	0.375	0.378
Calculated density (gm/cc)	7.578	7.573	7.695	7.705	7.616	7.759
Published density (gm/cc) ASTM	7.86	7.94	7.94	7.805	7.94	7.98
Calculated surface area (sq. cm)	23.995	23.561	22.843	23.162	23.766	22.859
Start date (MDY)	8/14/2013	8/14/2013	8/14/2013	8/14/2013	8/14/2013	8/14/2013
Start time (hours)	9:30	9:30	9:30	9:30	9:30	9:30
End date (MDY)	11/12/2013	11/12/2013	11/12/2013	11/12/2013	11/12/2013	11/12/2013
End time (hours)	10:30	10:30	10:30	10:30	10:30	10:30
Temperature (°C)	50	50	50	50	50	50
Exposure time (hours)	2161	2161	2161	2161	2161	2161
Ending weight (grams)	21.8838	21.7944	20.0156	21.3542	22.7807	20.0803
Loss in weight (grams)	0.006	0.0016	0.0006	0.0008	0.0013	0.0006
Rate of corrosion (mpy) using calculated density	0.0527	0.0143	0.0054	0.0072	0.0115	0.0054
Rate of corrosion (mpy) using published density	0.0508	0.0137	0.0053	0.0071	0.0110	0.0053

Table 3: 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
Phosphorus	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

Table 4: Metals in test fluid

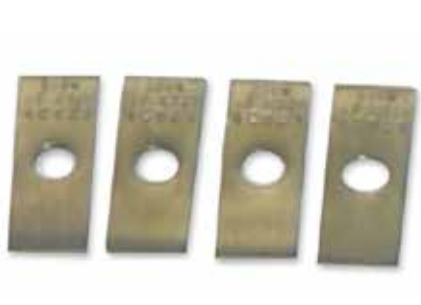
ICP analysis before and after 90-day vapor space corrosion rate study: C1018 coupon

Bottle was sealed but some slight water vapor loss may have occurred

Metal ID		Metals in sample Before	Metals in sample After at 50°C.	50°C Test Difference	
Ag	(Silver)	1.66	5.54	3.88	
Al	(Aluminum)	10.12	7.58	-2.54	
As	(Arsenic)	4.36	3.83	-0.53	
B	(Boron)	2.11	2.65	0.54	
Ba	(Barium)	3.40	7.46	4.06	
Be	(Beryllium)	0.13	1.13	1.00	
Bi	(Bismuth)	10.41	8.56	-1.85	
Cd	(Cadmium)	1.33	3.23	1.9	
Ce	(Cerium)	4.01	NA	—	
Co	(Cobalt)	2.09	3.57	1.48	
Cr(II)	(Chromium)	2.36	6.10	3.74	
Cu	(Copper)	0.54	1.09	0.55	
Fe(II)	(Iron)	1.66	3.42	1.76	Little to no increase in iron
K	(Potassium)	NA	NA	—	
La	(Lanthanum)	9.46	NA	—	
Li	(Lithium)	2.73	4.25	1.52	
Mg	(Magnesium)	570.37	854.44	284.07	
Mn	(Manganese)	1.58	4.26	2.68	
Mo	(Molybdenum)	4.04	8.23	4.19	
Na	(Sodium)	97.65	82.35	-15.3	
Ni	(Nickel)	2.14	1.93	-0.21	
Pb	(Lead)	12.74	4.88	-7.86	
Rb	(Rubidium)	0.34	1.98	1.64	
Sb	(Antimony)	1.28	2.86	1.58	
Se	(Selenium)	6.26	6.33	0.07	
Sn	(Tin)	7.05	4.01	-3.04	
Sr	(Strontium)	73.41	116.25	42.84	
Ti	(Titanium)	0.89	4.04	3.15	
Tl	(Thallium)	17.17	22.64	5.47	
U	(Uranium)	1.75	6.57	4.82	
V	(Vanadium)	13.85	21.28	7.43	
Zn(I)	(Zinc)	16.07	6.64	-9.43	

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 2: Test coupons before 90-day above surface exposure at 20 °C and 50 °C

C 1018	304W	316 LW
		

Duplex 2205	304 LW	316
		

Figure 3: Test coupons after 90-day above surface exposure at 20 °C still in test bottles (before cleaning)

Figure 3: Test coupons after 90-day above surface exposure at 50 °C still in test bottles (before cleaning)

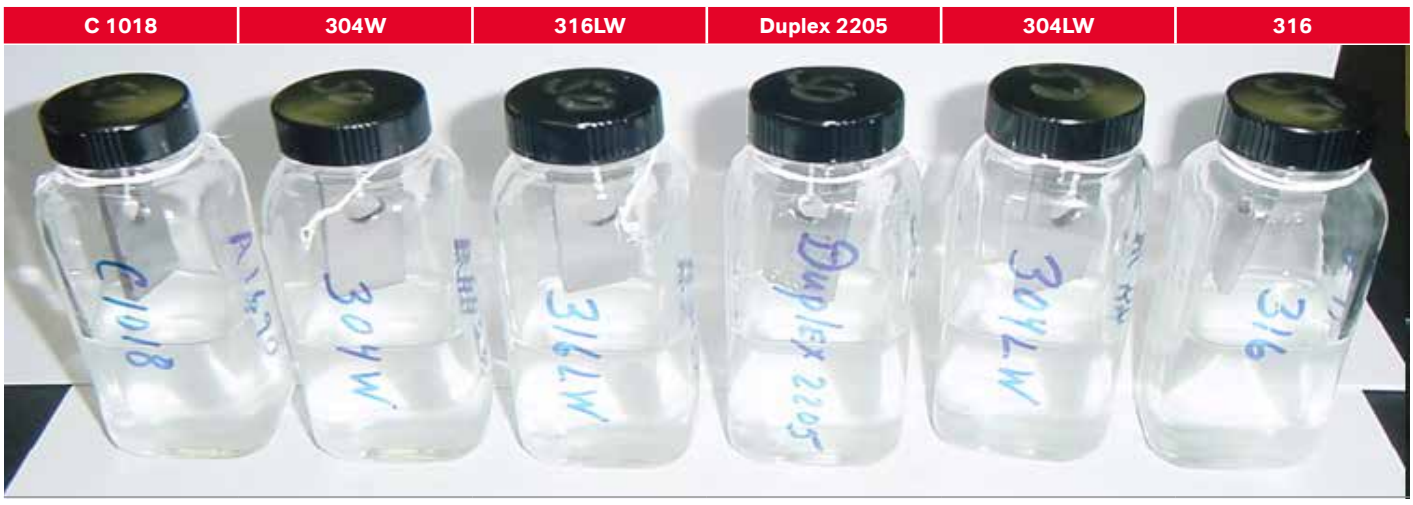


Figure 4: Test coupons after 90-day above surface exposure at 20 °C removed from test bottles (before cleaning)

C 1018	304W	316LW	Duplex 2205	304LW	316
					

Test coupons after 90-day above surface exposure at 50 °C removed from test bottles (before cleaning)

C 1018	304W	316LW	Duplex 2205	304LW	316
					

Figure 5: C1018 coupon after 90-day above surface exposure at 20 °C and 50 °C (before cleaning)

C1018 @ 20 °C	C1018 @ 50 °C
	

Figure 6: Test coupons after 90-day above surface exposure at 20 °C removed from test bottles (after cleaning)

C 1018	304W	316LW	Duplex 2205	304LW	316
					

Test coupons after 90-day above surface exposure at 50 °C removed from test bottles (after cleaning)

C 1018	304W	316LW	Duplex 2205	304LW	316
					

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