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Subject: Corrosion Studies on GeoBrom™ 520
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Notebook: Great Lakes Solutions 3455-102
Date: December 18, 2013

Background Information

A 90 day above surface corrosion rate study was requested using GeoBrom™ HG 520 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 iron, welded coupon
- 2205 → Duplex 2205 coupon
- 304-LW → 304SS, low iron, welded coupon
- 316 → 316SS coupon

Objectives of the Study

1. Establish above surface "vapor" corrosion rates at 20° C and 50° C for each metal.
2. Visually document coupon condition before and after 90 day exposure.

Executive Summary

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™ HG 520 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. 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 50° C and the second group 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 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; (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 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:

$$\text{Corrosion Rate} = (K \times W) / (A \times T \times D)$$

- 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

Table #1 and Table #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 and data presented within Figure #1.

GeoBrom™ HG 520 test solutions were saved for inductively coupled plasma (ICP) analysis before and after the immersion tests. After the 90 day period, all GeoBrom™ HG 520 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™ HG 520 used for the C-1018 coupon, since the C-1018 coupon had the highest corrosion rate after 90 days at 50° C. Table #4 notes 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. These are presented in Figures #2 to # 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 CaBr₂ depends on the application. These data are relevant only to the 52% CaBr₂ solution. Dilute solutions or other uses of 52% solution may exhibit different corrosive behaviors.

Figure #1 → Corrosion Rate Trend Chart w/ Y axis at 0 to 0.06 mpy scale

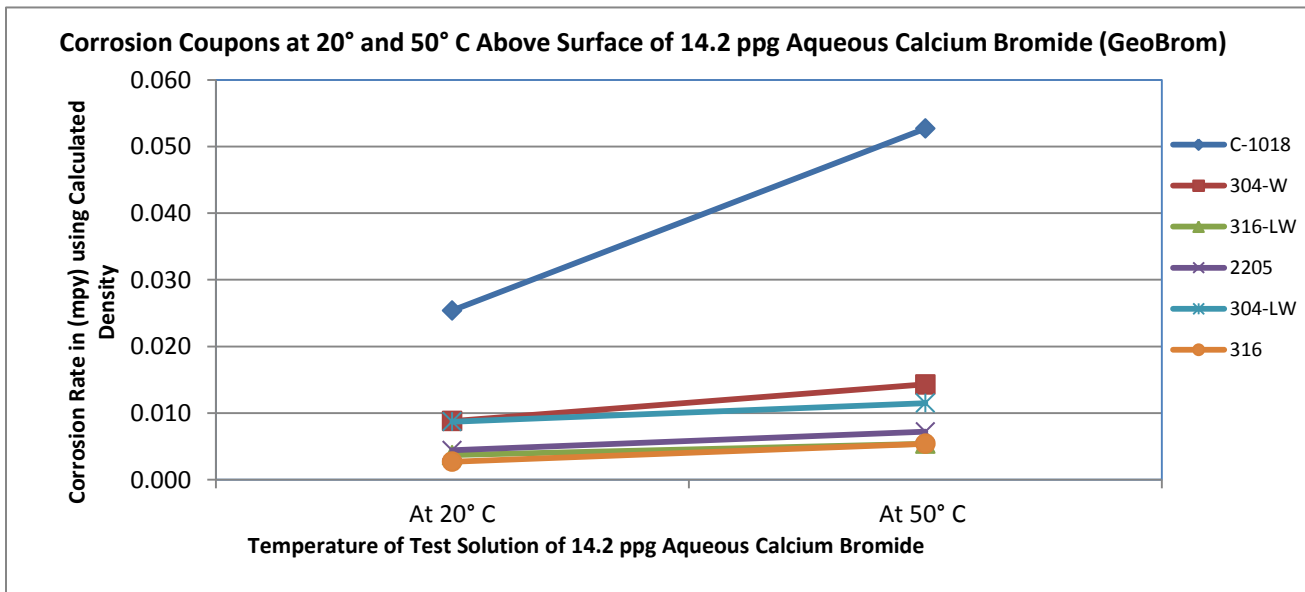


Table #1 Above Surface at 20° c

Corrosion Coupons Testing in PSL in GeoBrom 14.2 ppg Solution ==> Above Surface at 20° C

August 14, 2013 to November 12, 2013 T. G. Ray

Total exposure time was 90 days + 1hour

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
ID	A1689	A0027	A8156	five dot	A0016	A1167
Heat Code	HT H820	HT G729	AL 203	NA	HT G730	HT J550
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)	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
Date in Oven (MDY)	8/14/2013	8/14/2013	8/14/2013	8/14/2013	8/14/2013	8/14/2013
Time in oven (hours)	9:30	9:30	9:30	9:30	9:30	9:30
Date out of oven (MDY)	11/12/2013	11/12/2013	11/12/2013	11/12/2013	11/12/2013	11/12/2013
Time out of oven (hours)	10:30	10:30	10:30	10:30	10:30	10:30
Oven Temperature (°C)	50	50	50	50	50	50
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 Above Surface at 50° C

Corrosion Coupons Testing in PSL in GeoBrom 14.2 ppg Solution ==> Above Surface at 50° C

August 14, 2013 to November 12, 2013

T. G. Ray

Total exposure time was 90 days + 1 hour

Using ASTM Designation: G1 - 03 (reapproved 2011) Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens

	Duplex					
Coupon Type	C-1018	304-W	316-LW	2205	304-LW	316
ID	A1690	A0028	A8157	six dot	A0017	A1168
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)	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
Date in Oven (MDY)	8/14/2013	8/14/2013	8/14/2013	8/14/2013	8/14/2013	8/14/2013
Time in oven (hours)	9:30	9:30	9:30	9:30	9:30	9:30
Date out of oven (MDY)	11/12/2013	11/12/2013	11/12/2013	11/12/2013	11/12/2013	11/12/2013
Time out of oven (hours)	10:30	10:30	10:30	10:30	10:30	10:30
Oven 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

Metal Type	AISI = American Iron and Steel Institute				Data in % by weight	
	<u>AISI 1018</u>	<u>AISI 304</u>	<u>AISI 304-L</u>	<u>AISI 316</u>	<u>AISI 316-L</u>	<u>Duplex 2205</u>
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		18 - 20	18-20	16 - 18	17 - 18	21 - 23
Nickel		8 to 12	8 to 12	10 to 14	11 to 14	4.5 - 6.5
Molybdenum				2 to 3	3 to 3	2.5 - 3.5
Nitrogen		0.10 max	0.10 max			0.8 - 2.0
Iron	balance	balance	balance	balance	balance	balance

Table #4 Metals in Test Fluid

ICP Analysis Before and After 90 day Above Surface “Vapor” Corrosion Rate Study

All bottles were sealed but some slight water vapor loss may have occurred.

All results in mg/L		Metals in sample	Metals in sample	50° C Test	
<u>Metal ID</u>	<u>Before</u>	<u>after at 50° C.</u>	<u>Difference</u>		
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	

Figure #2 → Test Coupons before 90 day Above Surface exposure at 20° C and 50° C

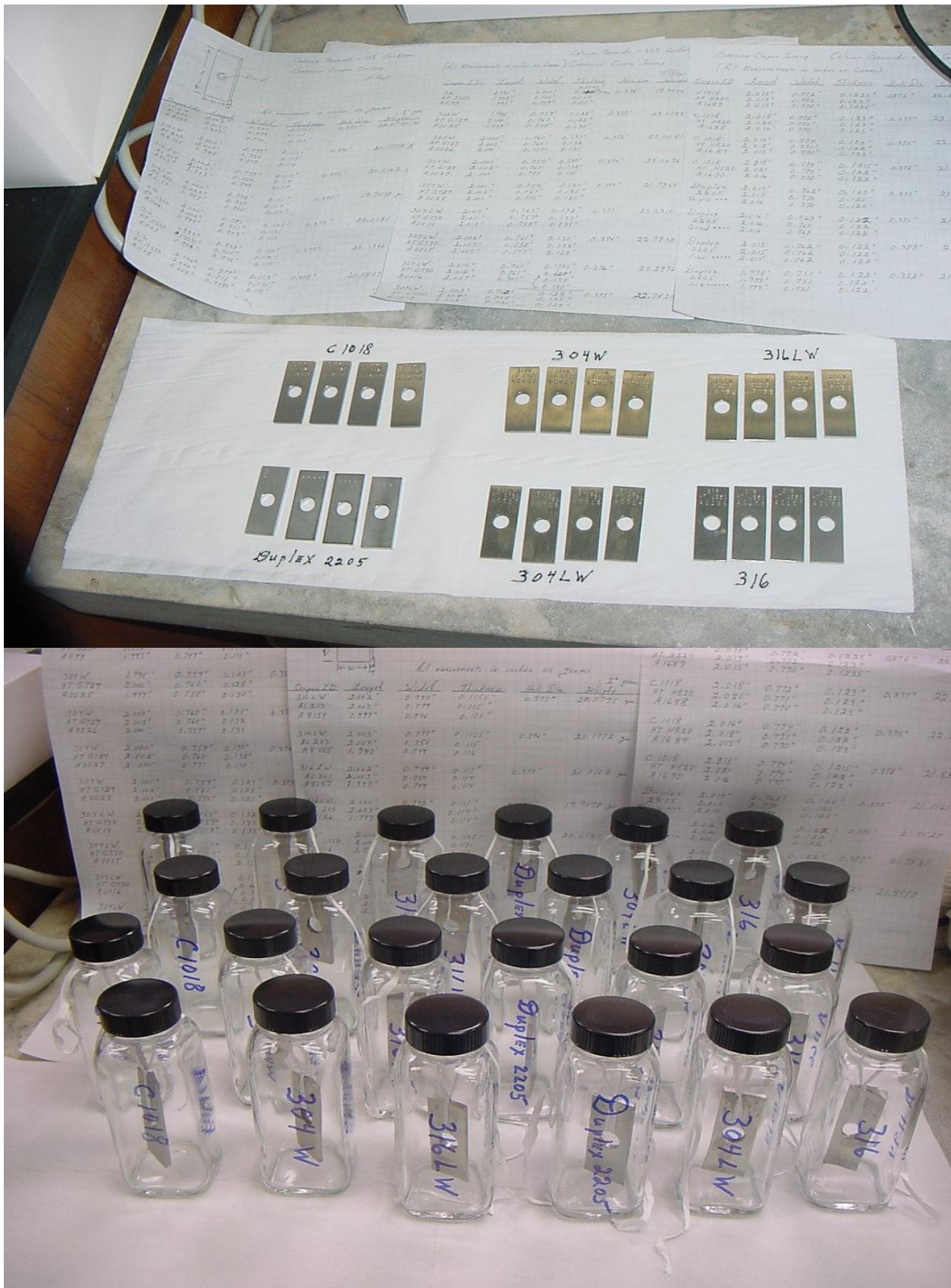


Figure #3 → Test Coupons after 90 day Above Surface exposure at 20° C and 50° C while still in Test Bottles (before cleaning)

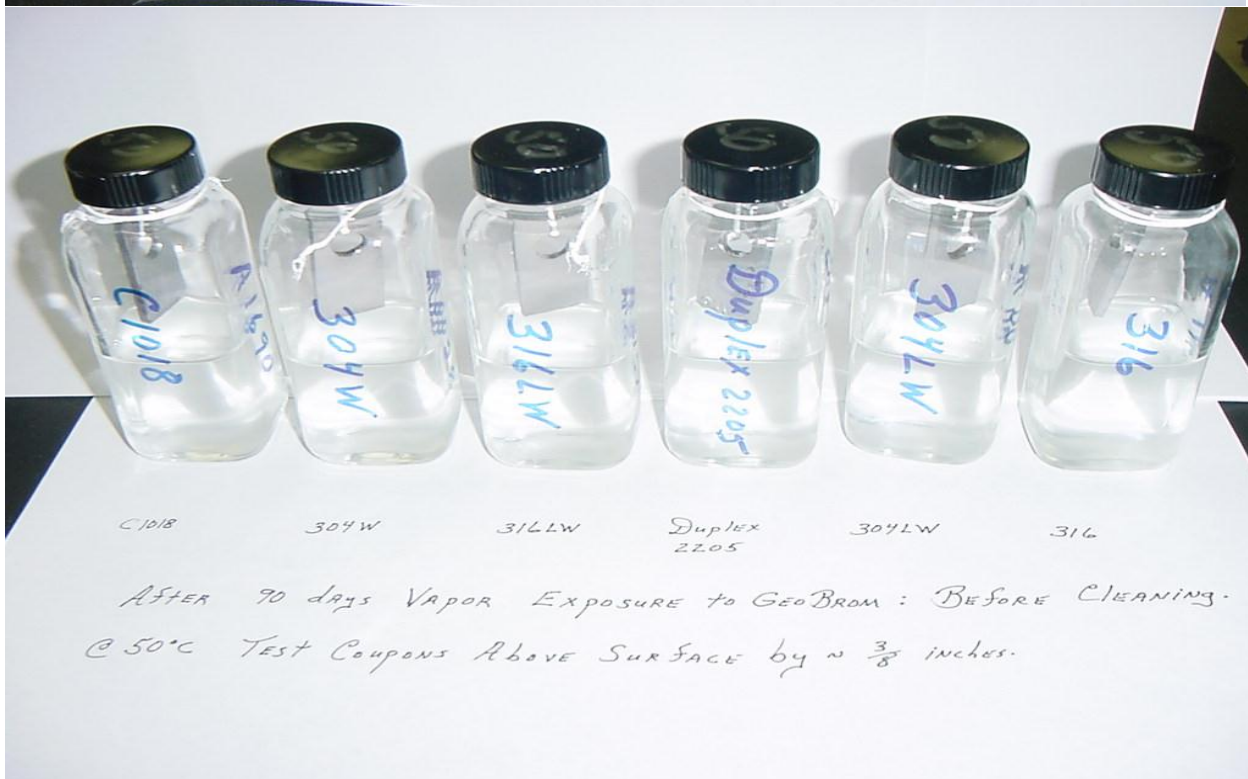


Figure #4 → Test Coupons after 90 day Above Surface exposure at 20° C and 50° C removed from Test Bottles (before cleaning)

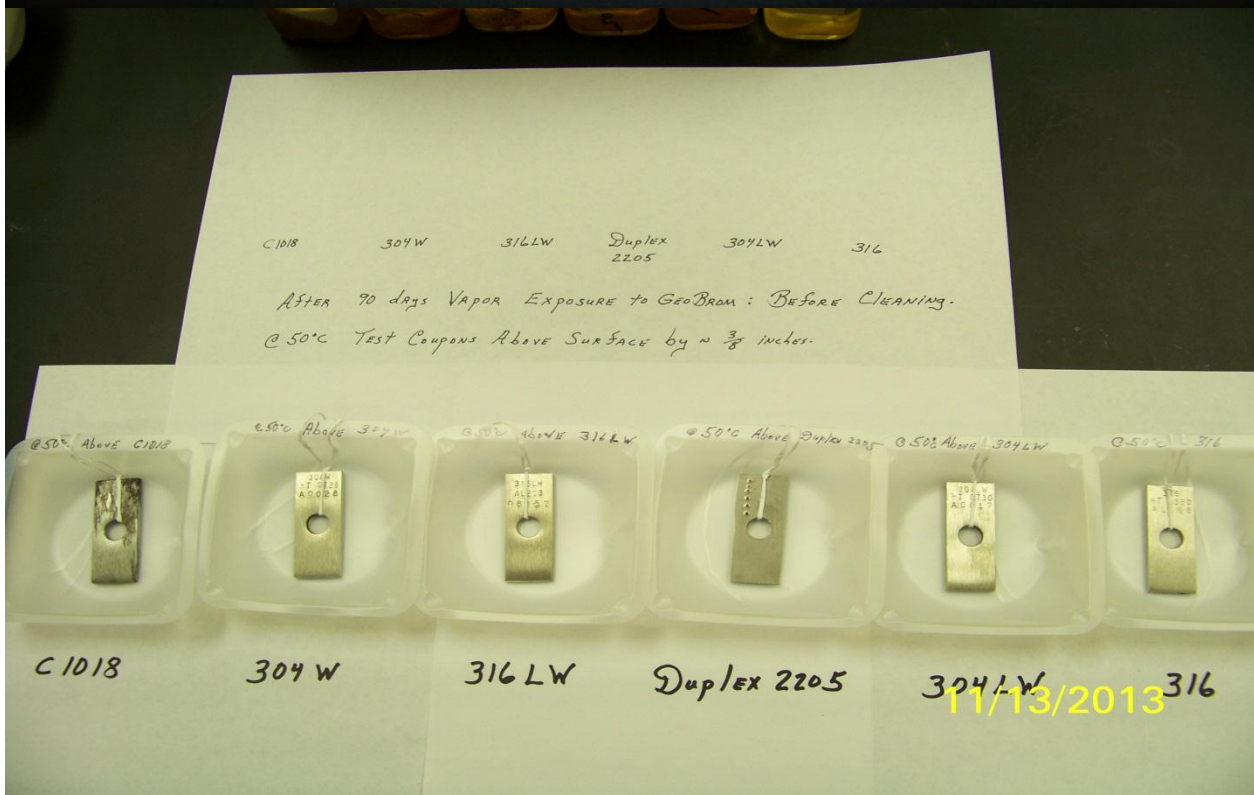
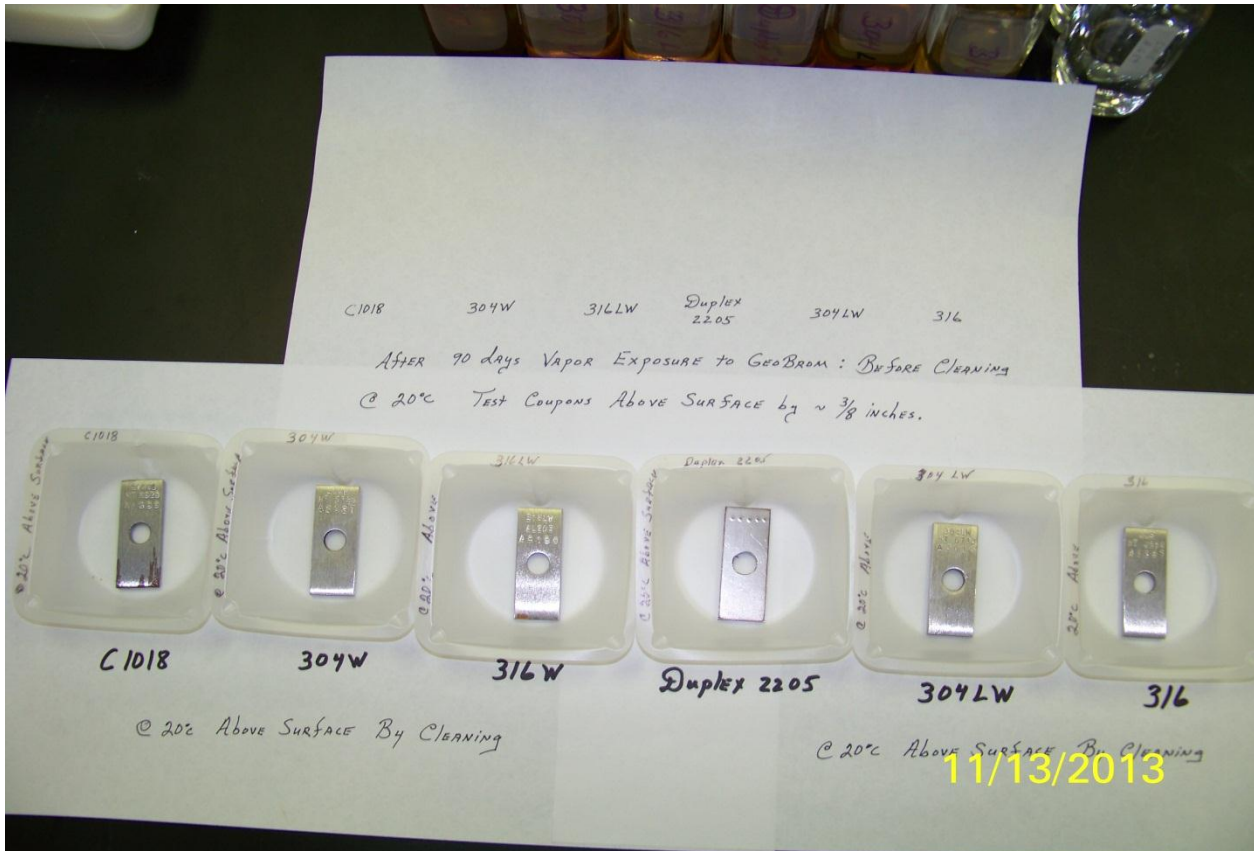


Figure #5 → C1018 Coupon after 90 day Above Surface exposure at 20° C and 50° C (before cleaning)

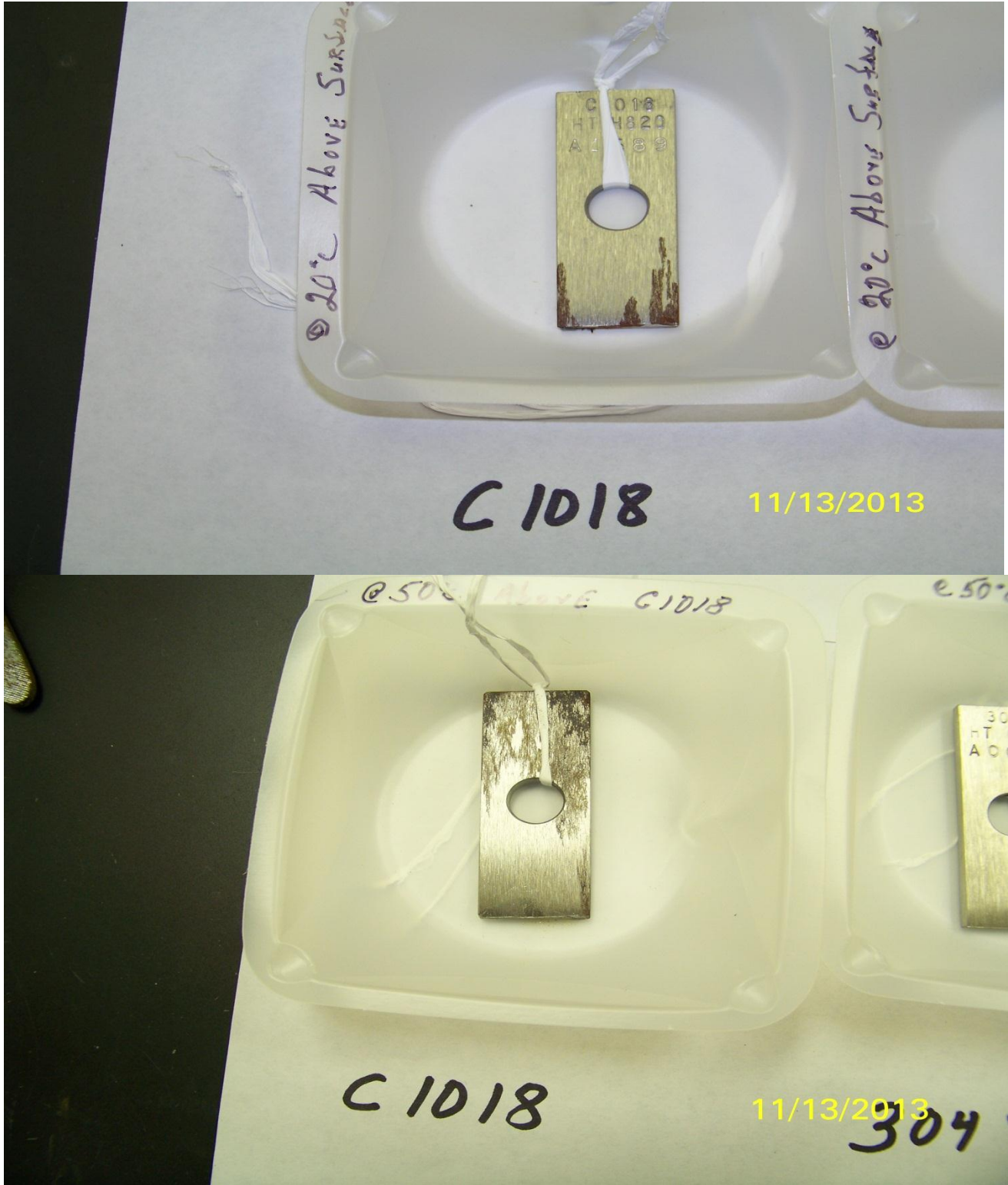


Figure #6 → Test Coupons after 90 day Above Surface exposure at 20° C and 50° C removed from Test Bottles (after cleaning)

