

**Condition Report
Record Report**

QA:QA

CR Num	CR Level	CR Type	Step Entry Date	Step	Step Resp	Step Owner
12868	B	QARD	6/1/2009 9:01:07 AM	Completed	N/A	N/A

Condition Information**CR Title:** Unexpected Test Results - Residue on Subset of Alloy 22 Coupons**Date Found:** 06-Oct-08**Time Found:** 15:11**CR Initiator:** Wall, Frederick**CR Initiating Org:** Sandia National Lab**Involve Initiator?** Yes**Condition Description:**

Inspection of Alloy 22 coupons exposed for 9.5 years in the LTCTF revealed that a subset of the coupons have a visually observable residue on the sample surfaces and adhered to the inside of the plastic bags used for sample storage. While it is possible that the residue is a deliquesced salt, it has a waxy consistency and may be an unexpected organic compound.

Initially, a single sample (DWA158) was identified as having evidence of a residue, and was documented on page 37 of SN-SNL-SCI-046-V3 on 9/22/2008. At the time of the observation the residue on this sample was not considered to be an unexpected test result - the condition of the samples removed from the LTCTF is somewhat variable and DWA158 was initially thought to lie within normal variations. Upon closer inspection of the residue that had been removed and archived during cleaning, it was determined that the substance was not representative of salt deposits that are typically found on coupons removed from the LTCTF.

It was considered due diligence to inspect the remaining uncleaned 9.5 year Alloy 22 coupons. A visual inspection was performed at SNL on 10/06/2008 and 40 out of 132 coupons, primarily from vessels 25 (SAW 60), 26 (SAW 90), and 30 (SDW 90), were identified that may also have some degree of residue. A follow-on inspection of other materials that had been exposed in vessels 25, 26, and 30 was performed at LLNL on 10/15/2008. Uncleaned metal coupons (primarily titanium and Alloys G3, C4, and I825) were visually inspected, and a subset of those samples was identified as possibly having similar residue.

At this time the composition of the residue has not been determined and no trends have yet been identified that clearly indicate the source of the residue. Therefore, it is not known if the residue is a natural byproduct of the chemical exposure and resulting corrosion processes or if it is a contaminant. An objective of this CR is to ensure that the 9.5 year Alloy 22 coupons having the residue are appropriately identified and tracked such that any influence on the weight-loss measurements and derived corrosion rates can be properly documented. The impact beyond potentially adding uncertainty to the corrosion rates for the 9.5 year Alloy 22 coupons has not been determined.

Supplemental Information:

**Condition Report
Record Report**

CR Num	CR Level	CR Type	Step Entry Date	Step	Step Resp	Step Owner
12868	B	QARD	6/1/2009 9:01:07 AM	Completed	N/A	N/A

Routing Notes:

10/22/08 Danika Miller - This CR has been prescreened by a member of the CAP Staff using criteria Technical Information.

Trend Only? No

Requirement Involved? Yes
Requirement: SCI-PRO-002Business Process:
Business Process ID:**Condition Information****Assignment Information**

Ownership Organization:	Sandia National Lab	Oversight Organization:	OTM - Sci Division
Responsible Organization:	Sandia National Lab	Oversight Lead:	Fish, Robert
Business Process Review Org:		QA Review Type:	No QA Review Required
		Quality Assurance Rep (QAR):	

Assignment Information**Screening Information**

CR Level: B	Date Submitted: 10/21/2008	Date Issued: 10/23/2008
CST / MRC Conclusions: 10/23/08 Danika Miller - Significance Determination established at a Level B using criteria definition and Technical Information.		

Screening Information**Review Information**

**Condition Report
Record Report**

CR Num	CR Level	CR Type	Step Entry Date	Step	Step Resp	Step Owner
12868	B	QARD	6/1/2009 9:01:07 AM	Completed	N/A	N/A

NRC Reportability Review (e.g. Part 21 and 10CFR63.73b)

Potential NRC Reportable CR? No

Validated NRC Reportable CR?

NRC Reportable Discussion:

Self-Revealing Conditions

* Conditions identified outside of formal processes (such as Self Assessments) where the event/consequence occurred prior to entry of the condition into CAP

Self-Revealing condition? No

10CFR835 - Radiological Protection Program (RPP) Review

Potential RPP issue? No

Validated RPP issue?

RPP Category:

RPP Discussion:

10CFR851 - Worker Safety and Health Program (WSHP) Review

Potential WSHP issue? No

Validated WSHP issue?

WSHP Category:

WSHP Discussion:

Occurrence Reporting and Processing System (ORPS) Review

Potential ORPS issue? No

Validated ORPS issue?

ORPS Criteria:

ORPS Significance:

ORPS Report ID:



OCRWM Corrective Action Program
**Condition Report
Record Report**



CR Num	CR Level	CR Type	Step Entry Date	Step	Step Resp	Step Owner
12868	B	QARD	6/1/2009 9:01:07 AM	Completed	N/A	N/A

ORPS Discussion:**NTS Reportable conditions only**

NTS Report ID:

Review Information**Evaluation Information****Immediate/Interim Action Taken?** Yes**Immediate/Interim Action Desc:**

11/21/08 - B. Mitcheltree - The immediate action is listed in the Cause Analysis, see attached file "Cause Analysis for CR 12868.pdf".

Previous Occurrence Review:

11/21/08 - B. Mitcheltree - The previous occurrence can be found in attached file "Cause Analysis for CR 12868.pdf".

Extent of Condition:

11/21/08 - B. Mitcheltree - The Extent of Condition can be found in attached file "Cause Analysis for CR 12868.pdf".

Evaluation Information**Cause Analysis Information****Cause Analysis Type:** Apparent Cause**Cause Analysis Results:**

11/21/08 - B. Mitcheltree - The Cause Analysis can be found in attached file "Cause Analysis for CR 12868.pdf".

LL/GI Required? Yes**Reason LL/GI Not Performed:****Cause Analysis Team Members**

Team Member Name

Team Member Organization



Condition Report Record Report



CR Num	CR Level	CR Type	Step Entry Date	Step	Step Resp	Step Owner
12868	B	QARD	6/1/2009 9:01:07 AM	Completed	N/A	N/A

Gromny, Jeffrey	Sandia National Lab
Russell, Michael	Sandia National Lab
Persoff, Peter	Sandia National Lab
Mitcheltree, Brian	Sandia National Lab

Cause Code(s):

- A2B4 - Equipment/Material Problem - Material Control LTA
- A2B6 - Equipment/Material Problem - Defective, Failed or Contaminated
- A4B3 - Management Problem - Work Organization/Planning LTA

Event Code(s):

- 1TC - Test Control Program
- 2ME - M&TE

Cause Analysis Information**Plan Information**

Plan Due Date: 11/22/2008	Original Est Comp Date: 5/27/2009	Date Completed: 5/28/2009
Plan Completed Date: 11/21/2008	Current Est Comp Date: 5/27/2009	Date Closed: 6/1/2009

Actions Required? Yes

Effectiveness Rev Required? No Effectiveness Rev Days

Corrective Action Plan Summary:

11/21/08 - B. Mitcheltree -

1) Test the residue on the samples more thoroughly to determine if it is consistent with a biofilm (bacteria activity). The additional testing may reveal the origin of the hydrocarbon residue. Action 12868-001

2) Confirm the composition of all vessels and racks because the investigation revealed that if the pH was 12 or above, a different type of material was supposed to be used. None of these solution reached that level (10.8 appears to be the highest), but it is possible that the different material was used in the highest pH scenario to provide operational margin. Action 12868-002

3) Compare a population of samples that contains a small amount of the residue to a population of samples that contains a large amount. The comparison is to determine if the calculated corrosion rate (based on measured mass change) of a sample is affected by the presence of the residue. This action will be a key to evaluating the impact of this CR. If it is determined that the residue has no impact on the calculated corrosion rates of the samples, this condition is still an unexpected test result and should be documented to prevent reoccurrence. Then the impact is minimal. If the additional investigations conclude that



OCRWM Corrective Action Program
Condition Report
Record Report



CR Num	CR Level	CR Type	Step Entry Date	Step	Step Resp	Step Owner
12868	B	QARD	6/1/2009 9:01:07 AM	Completed	N/A	N/A

the corrosion rates are affected by the hydrocarbon residue or if the analysis is inconclusive, then the CR will have to be replanned to revise the appropriate documents, which could include the SAR and TSPA. Action 12868-003

4) Revise the Long Term Corrosion Testing Plan to prevent reoccurrence.

Discussed Plan with CR Initiator? Yes **Discussion Results:** 11/21/08 - B. Mitchelltree - The initiator agreed with the plan.

Discussed Implementation with CR Initiator? Yes **Discussion Results:** 5/28/09- Initiator agrees with CR resolution.

Action	Title
12868-001	Test hydrocarbon residue
12868-002	Confirm the composition of the vessels
12868-003	Compare samples with large quantities versus small quantities of residue
12868-004	Revise the Long Term Corrosion Testing Plan

Plan Information

Review Information

Supv Review Plan

Step Completion Date	Person that performed review	Plan Approval Indicator and Comments, if any
11/21/2008 4:55:38 PM	Brown, Neil	Yes I have reviewed the causal analysis and agree that it meets all requirements and is sufficient to address this CR. I have reviewed the plan and concur that it requires all necessary and sufficient actions to resolve the condition. Neil Brown 11/21/08

MRC Review Plan

Step Completion Date	Person that performed review	Plan Approval Indicator and Comments, if any
12/10/2008 2:55:47 PM	Harding, Michelle	Yes 12/10/08 M. Harding - CR Plan/Apparent Cause reviewed and approved by the MRC on 12/10/08. The MRC has directed that upon completion of the evaluation, the responsible organization present the results to the MRC and has deferred determination on whether an effectiveness review is warranted until the evaluation is complete.

Oversee Implementation

Step Completion Date	Person that performed review	Implementation Done Indicator and Comments, if any
----------------------	------------------------------	--



Condition Report Record Report



CR Num 12868	CR Level B	CR Type QARD	Step Entry Date 6/1/2009 9:01:07 AM	Step Completed	Step Resp N/A	Step Owner N/A
-----------------	---------------	-----------------	--	-------------------	------------------	-------------------

Oversee Implementation (continued)

Step Completion Date	Person that performed review	Implementation Done Indicator and Comments, if any
----------------------	------------------------------	--

5/28/2009 3:17:58 PM	Mitcheltree, Wendy	<p>Yes 5/28/09 W. Mitcheltree: There were four actions associated with this CR. All four actions have been completed as follows: Action 12868-001: this completed action was to test the residue on the samples more thoroughly to determine if it is consistent with a biofilm (bacteria activity). A report was completed under the file: YM_alam_Celina_finalreport.doc which documented the fact that there was no evidence of nitrogen bonded to carbon ruling out the possibility of a biofilm. Action 12868-002: this completed action was to confirm the composition of all vessels and racks and investigate if there is a correlation between the stirring motors maintenance records and quantities of residue. It was determined that this action is no longer necessary as the vessel or rack degradation was not the cause of the residue on the samples. The residue has been confirmed to be a long-chain molecule consistent with a lubricant (as documented in Action 12868-001). The composition of the vessels and the racks has no bearing on the result of this CR or the origin of the residue. Action 12868-003: this completed action was to compare a population of samples that contains a small amount of the residue to a population of samples that contains a large amount. The 9.5 year uncleaned samples were examined to find a set of samples with similar exposure conditions and varying levels of organic residue. The samples were then analyzed for organic coverage as using infrared spectroscopy (file: FTIR09007 03_13_09.doc). After determining the quantity of organics the samples were then cleaned to determine the corrosion rates. As shown in file FTIR vs Mass Loss.xls no adverse trend associated with the quantity of organic residue was observed. Action 12868-004: this completed action was to revise the Long Term Corrosion Testing Plan to include a Lesson Learned to discuss this CR and how the proper planning could have avoided this CR. The Long Term Corrosion Testing Plan (SAND2009-0923) has been revised and a lesson learned was included the accession number for this Plan is LLR.20090305.0199. All four action associated with CR 12868 have been completed this CR should be considered closed.</p>
----------------------	--------------------	---



OCRWM Corrective Action Program
**Condition Report
 Record Report**



CR Num	CR Level	CR Type	Step Entry Date	Step	Step Resp	Step Owner
12868	B	QARD	6/1/2009 9:01:07 AM	Completed	N/A	N/A

Oversee Implementation (continued)

Step Completion Date	Person that performed review	Implementation Done Indicator and Comments, if any
----------------------	------------------------------	--

In regards, to the immediate actions, the Engineered System Integration Responsible Manager lifted the ban on the cleaning of the LTCTF samples that may be impacted by the residue. As for the DTNs that were impacted by this CR, they were already behind the firewall due to actions associated with CR 11851 and will currently remain so, and will be addressed by CR11851. As far as this CR is concerned the data is considered adequate.

Supv Verify Impl

Step Completion Date	Person that performed review	CR Verification Indicator / Comments
----------------------	------------------------------	--------------------------------------

5/29/2009 2:30:55 PM	Brown, Neil	
----------------------	-------------	--

Yes I have reviewed the work performed to date and concur that all actions have been completed. The available information provides a high level of confidence that the unexpected organic residue did not act to decrease the corrosion rates and thus is unlikely to impact the corrosion models, TSPA, or the SAR. Therefore this CR should be closed.

However, due to the nature of this CR, experimental uncertainties and the facts that the contaminant was introduced at least 10 years ago and that the samples have been subsequently handled, it cannot be declared with certainty that the unintended organic residue had no effect. CR 13795 "Opportunity for Improvement Corrosion Model Defensibility" has been opened as a result of this CR and others to indicate an opportunity for improvement to increase the defensibility of the corrosion models.

Note this CR should be closed on its own and is not being closed to CR 13795.

Neil Brown 5/29/09

Review Information

CRRecordReport



Condition Report Record Report



CR Num	CR Level	CR Type	Step Entry Date	Step	Step Resp	Step Owner
12868	B	QARD	6/1/2009 9:01:07 AM	Completed	N/A	N/A

CR Step History

Rev #	EnteredStep	Entry Date	Step Owner	Step Resp	Exit Date	Exit To Status	User that hit 'GO'	Milestone on Exit	# of Days in Step
1	Initiate CR	10/9/2008	Bonano, Evaristo	Wall, Frederick	10/21/2008	Staff Review CR	Wall, Frederick		12
2	Staff Review CR	10/21/2008	Giacomini, Michael	Miller, Danika	10/22/2008	CST Review CR	Miller, Danika		1
3	CST Review CR	10/22/2008	Giacomini, Michael	Miller, Danika	10/23/2008	Plan CR	Miller, Danika	CR ISSUED 10/23/2008 1:27:29 PM	1
4	Plan CR	10/23/2008	Bonano, Evaristo	Mitcheltree, Brian	11/21/2008	Supv Review Plan	Mitcheltree, Brian		29
5	Supv Review Plan	11/21/2008	Bonano, Evaristo	Brown, Neil	11/21/2008	MRC Review Plan	Brown, Neil	PLAN COMPLETED 11/21/2008 4:55:38 PM	0
6	MRC Review Plan	11/21/2008	Giacomini, Michael	Harding, Michelle	12/10/2008	Oversee Implementation	Harding, Michelle		19
7	Oversee Implementation	12/10/2008	Bonano, Evaristo	Mitcheltree, Wendy	5/28/2009	Supv Verify Impl	Mitcheltree, Wendy	CAs COMPLETED 5/28/2009 3:17:58 PM	169
8	Supv Verify Impl	5/28/2009	Bonano, Evaristo	Brown, Neil	5/29/2009	CST Close CR	Brown, Neil		1
9	CST Close CR	5/29/2009	Pesek, John	Miller, Danika	6/1/2009	Completed	Miller, Danika	CR CLOSED 6/1/2009 9:01:07 AM	3
10	Completed	6/1/2009	N/A	N/A					N/A

CR Step History**CR Attachments**

Filename	Size	Date
Cause Analysis for CR 12868.pdf	918 kb	
CR 12868 - Part 21.pdf	8077 kb	
CR 12868 Closure Checklist.doc	85 kb	

CR Attachments



OCRWM Corrective Action Program
Condition Report
Record Report
 Corrective Action Report



CR Num 12868	Action Num 12868-001	Step Entry Date 5/28/2009 3:15:44	Step Completed	Step Resp N/A	Step Owner N/A
-----------------	-------------------------	--------------------------------------	-------------------	------------------	-------------------

Action Details

Action Number:	12868-001	Current Due Date: 5/19/2009	Date Completed: 5/27/2009	Date Closed: 5/28/2009
		Original Due Date: 3/11/2009		

Accepting Org:	Sandia National Lab	<i>Bonano, Evaristo</i>
Assigned To Org:	Sandia National Lab	<i>Bonano, Evaristo</i>

Action Title: Test hydrocarbon residue

Action Description:

11/21/08 - B. Mitcheltree - Test the residue on the samples more thoroughly to determine if it is consistent with a biofilm (bacteria activity). The additional testing may reveal the origin of the hydrocarbon residue.

Objective evidence will be the results of this test or justification why this was not performed.

Action Taken:

5/28/09- W. Mitcheltree: The action was to test the residue on the samples more thoroughly to determine if it is consistent with a biofilm (bacteria activity). If it is a biofilm additional testing may reveal the origin of the hydrocarbon residue.

As shown in the attached report (YM_alam_Celina_finalreport.doc) entitled "Analysis of organic deposit on Alloy 22 Coupons", dated 3/20/2009 there is no evidence of nitrogen bonded to carbon in the organic residue ruling out the possibility of a biofilm (protein containing deposit). Therefore, the organic residue is not a biofilm and this action has been completed and should be closed. Also, this same report demonstrates that the molecular weight of the organic residue is too high to be from degradation or extraction from the tank liner and most likely originates from a lubricant, grease or similar source (This is also addressed in Action 002). The objective evidence is the attached file YM_alam_Celina_finalreport.doc

Routing Notes:

Action Details
Action Adjustments

Adjustment Num	Adjustment Title	Proposed Due Date	Step
12868-001-001	Due Date Adjustment	5/19/2009	Completed

**Condition Report
Record Report**

Corrective Action Report



CR Num 12868	Action Num 12868-001	Step Entry Date 5/28/2009 3:15:44	Step Completed	Step Resp N/A	Step Owner N/A
------------------------	--------------------------------	---	--------------------------	-------------------------	--------------------------

Action Adjustments**Action Step History**

Rev #	EnteredStep	Entry Date	Step Owner	Step Resp	Exit Date	Exit To Status	User that hit 'GO'	# of Days in Step
<u>1</u>	Plan Action	11/21/2008	Bonano, Evaristo	Mitcheltree, Brian	11/21/2008	Perform Action	Mitcheltree, Brian	0
<u>2</u>	Perform Action	11/21/2008	Bonano, Evaristo	Mitcheltree, Wendy	5/28/2009	Completed	Mitcheltree, Wendy	188
<u>3</u>	Completed	5/28/2009	N/A	N/A				N/A

Action Step History**Action Attachments**

Filename	Size	Date
YM Alam Celina finalreport.doc	562 kb	

Action Attachments



Condition Report

Record Report

Corrective Action Report



CR Num	Action Num	Step Entry Date	Step	Step Resp	Step Owner
12868	12868-002	3/30/2009 3:32:34	Completed	N/A	N/A

Action Details

Action Number:	12868-002	Current Due Date: 3/25/2009	Date Completed: 3/30/2009	Date Closed: 3/30/2009
		Original Due Date: 3/25/2009		

Accepting Org:	Sandia National Lab	<i>Bonano, Evaristo</i>
Assigned To Org:	Sandia National Lab	<i>Bonano, Evaristo</i>

Action Title: Confirm the composition of the vessels

Action Description:

11/21/08 - B. Mitcheltree - Confirm the composition of all vessels and racks because the investigation revealed that if the pH was 12 or above, a different type of material was supposed to be used. None of these solution reached that level (10.8 appears to be the highest), but it is possible that the different material was used in the highest pH scenario to provide operational margin. And investigate if there is a correlation between the stirring motors maintenance records and quantities of residue.

Objective evidence will be the results of this investigations or justification why this was not performed.

Action Taken:

3/30/09 - B. Mitcheltree - As a result of action 12868-001, this action is no longer necessary as the vessel or rack degradation was not the cause of the residue on the samples. The residue has been confirmed to be a long-chain molecule consistent with a lubricant. The composition of the vessels and the racks has no bearing on the result of this CR or the origin of the residue.

There is insufficient information to enable testing to determine a correlation between maintenance and quantities of residue. As a result of Action 12868-003, the quantities of residue on the sample had minimal or no impact on the corrosion rates. There is no reason to pursue this action any further because of the conclusions from actions 001 and 003 (see those actions for additional discussion).

Routing Notes:

Action Details

Action Adjustments

Adjustment Num	Adjustment Title	Proposed Due Date	Step
< NO ADJUSTMENTS LINKED TO THIS CORRECTIVE ACTION >			



Condition Report Record Report

Corrective Action Report



CR Num 12868	Action Num 12868-002	Step Entry Date 3/30/2009 3:32:34	Step Completed	Step Resp N/A	Step Owner N/A
------------------------	--------------------------------	---	--------------------------	-------------------------	--------------------------

Action Adjustments

Action Step History

<i>Rev #</i>	<i>Entered Step</i>	<i>Entry Date</i>	<i>Step Owner</i>	<i>Step Resp</i>	<i>Exit Date</i>	<i>Exit To Status</i>	<i>User that hit 'GO'</i>	<i># of Days in Step</i>
<u>1</u>	Plan Action	11/21/2008	Bonano, Evaristo	Mitcheltree, Brian	11/21/2008	Perform Action	Mitcheltree, Brian	0
<u>2</u>	Perform Action	11/21/2008	Bonano, Evaristo	Mitcheltree, Brian	3/30/2009	Completed	Mitcheltree, Brian	129
<u>3</u>	Completed	3/30/2009	N/A	N/A				N/A

Action Step History

Action Attachments

Filename	Size	Date
< NO ATTACHMENTS LINKED TO THIS CORRECTIVE ACTION >		

Action Attachments



OCRWM Corrective Action Program
Condition Report
Record Report
 Corrective Action Report



CR Num 12868	Action Num 12868-003	Step Entry Date 5/28/2009 3:16:28	Step Completed	Step Resp N/A	Step Owner N/A
-----------------	-------------------------	--------------------------------------	-------------------	------------------	-------------------

Action Details

Action Number:	12868-003	Current Due Date: 5/19/2009	Date Completed: 5/27/2009	Date Closed: 5/28/2009
		Original Due Date: 4/15/2009		

Accepting Org:	Sandia National Lab	Bonano, Evaristo
Assigned To Org:	Sandia National Lab	Bonano, Evaristo

Action Title: Compare samples with large quantities versus small quantities of residue

Action Description:

11/21/08 - B. Mitcheltree - Compare a population of samples that contains a small amount of the residue to a population of samples that contains a large amount. The comparison is to determine if the calculated corrosion rate (based on measured mass change) of a sample is affected by the presence of the residue. This action will be a key to evaluating the impact of this CR. If it is determined that the residue has no impact on the calculated corrosion rates of the samples, this condition is still an unexpected test result and should be documented to prevent reoccurrence. Then the impact is minimal. If the additional investigations conclude that the corrosion rates are affected by the hydrocarbon residue or if the analysis is inconclusive, then the CR will have to be replanned to revise the appropriate documents, which could include the SAR and TSPA.

Action Taken:

5/28/09 W. Mitcheltree: The action was to compare a population of samples that contains a small amount of the residue to a population of samples that contains a large amount.

The 9.5 year uncleaned samples were examined to find a set of samples with similar exposure conditions and varying levels of organic residue. The 9.5 year SCW Aqueous 60C samples were qualitatively judged to be the most appropriate samples for this comparison. The samples were then analyzed for organic coverage as using infrared spectroscopy (attached file: FTIR09007 03_13_09.doc). After determining the quantity of organics the samples were then cleaned to determine their respective corrosion rates. As shown in file FTIR vs Mass Loss.xls the corrosion rate showed a trend of higher corrosion rates with increasing quantity of organic residue. The trend correlation is weak, however, as documented by statistical analyses that show almost a 20% chance that randomly obtained data would fit the linear equation as well as the data. The analysis did not account for measurement uncertainties in the corrosion rates and organic layer thickness, and spatial variability in the organic layer thickness. In addition, the analyses could not account for organics removed during sample rinsing and storage. Therefore, the most appropriate characterization of the analysis is that no adverse trend is associated with the organic residue. Therefore, it is concluded that the organic residue does not impact the conclusions of the general corrosion model, the TSPA or the SAR. The objective evidence is contained in the following files attached to the action: FTIR 09007 03_13_09.doc, and FTIR vs Mass Loss.xls.

Also, an action was taken in Action-004 to prevent reoccurrence on unexpected test results via Long Term Corrosion Testing Plan (SAND2009-0923).



Condition Report

Record Report

Corrective Action Report



CR Num 12868	Action Num 12868-003	Step Entry Date 5/28/2009 3:16:28	Step Completed	Step Resp N/A	Step Owner N/A
------------------------	--------------------------------	---	--------------------------	-------------------------	--------------------------

Routing Notes:

Action Details

Action Adjustments

Adjustment Num 12868-003-001	Adjustment Title Due Date Adjustment	Proposed Due Date 5/19/2009	Step Completed
--	--	---------------------------------------	--------------------------

Action Adjustments

Action Step History

Rev #	EnteredStep	Entry Date	Step Owner	Step Resp	Exit Date	Exit To Status	User that hit 'GO'	# of Days in Step
1	Plan Action	11/21/2008	Bonano, Evaristo	Mitcheltree, Brian	11/21/2008	Perform Action	Mitcheltree, Brian	0
2	Perform Action	11/21/2008	Bonano, Evaristo	Mitcheltree, Wendy	5/28/2009	Completed	Mitcheltree, Wendy	188
3	Completed	5/28/2009	N/A	N/A				N/A

Action Step History

Action Attachments

Filename	Size	Date
FTIR vs Mass Loss.xls	60 kb	
FTIR09007 03_13_09.doc	330 kb	

Action Attachments



Condition Report Record Report

Corrective Action Report



CR Num	Action Num	Step Entry Date	Step	Step Resp	Step Owner
12868	12868-004	3/12/2009 2:58:28	Completed	N/A	N/A

Action Details

Action Number:	12868-004	Current Due Date: 5/20/2009	Date Completed: 3/12/2009	Date Closed: 3/12/2009
		Original Due Date: 5/20/2009		

Accepting Org:	Sandia National Lab	<i>Bonano, Evaristo</i>
Assigned To Org:	Sandia National Lab	<i>Bonano, Evaristo</i>

Action Title: Revise the Long Term Corrosion Testing Plan

Action Description:

11/21/08 - B. Mitcheltree - Revise the Long Term Corrosion Testing Plan to include a Lesson Learned to discuss this CR and how the proper planning could have avoided this issue.

Also make consideration for the following three concerns:

1. Future corrosion testing environment sterile or devoid of nutrients that would promote biological activity, this could include but not limited to: the use of UV light and additives to the solution. (pending confirmation that it is a biofilm)
2. Use of better materials that would not degrade at the temperature, pH, and water chemistry envisioned for each testing environment.
3. Prevention of oil/lubricate leaking into the solutions.

Action Taken:

3/12/09 - B. Mitcheltree - The Long Term Corrosion Testing Plan (SAND2009-0923) has been revised and a lesson learned was included that discusses this CR and how the proper planning could have avoided this issue. The accession number for this Plan is LLR.20090305.0199.

Routing Notes:

Action Details

Action Adjustments

Adjustment Num	Adjustment Title	Proposed Due Date	Step
< NO ADJUSTMENTS LINKED TO THIS CORRECTIVE ACTION >			



Condition Report Record Report

Corrective Action Report



CR Num
12868

Action Num
12868-004

Step Entry Date
3/12/2009 2:58:28

Step
Completed

Step Resp
N/A

Step Owner
N/A

Action Adjustments

Action Step History

Rev #	Entered Step	Entry Date	Step Owner	Step Resp	Exit Date	Exit To Status	User that hit 'GO'	# of Days In Step
1	Plan Action	11/21/2008	Bonano, Evaristo	Mitcheltree, Brian	11/21/2008	Perform Action	Mitcheltree, Brian	0
2	Perform Action	11/21/2008	Bonano, Evaristo	Mitcheltree, Brian	3/12/2009	Completed	Mitcheltree, Brian	111
3	Completed	3/12/2009	N/A	N/A				N/A

Action Step History

Action Attachments

Filename

Size

Date

< NO ATTACHMENTS LINKED TO THIS CORRECTIVE ACTION >

Action Attachments



Condition Report

Record Report

CA Adjustment Report



CR Num	Action Num	Action Adj Num	Step Entry Date	Step	Step Resp	Step Owner
12868	12868-001	12868-001-001	3/30/2009 4:10:11	Completed	N/A	N/A

Action Adjustment Details

Adjustment Number: 12868-001-001

Requested Due Date: 5/19/2009

Date Request Submitted: 3/30/2009

Date Closed: 3/30/2009

Adjustment Title: Due Date Adjustment

Reason for Adjustment:

3/30/09 - B. Mitcheltree - As a result of many RAIs from the NRC, the schedule for this CR has suffered.

Adjustment Response:

I concur with this action adjustment. To date the corrosion team has completed 34 RAIS with 10 more due 4/13/09. Neil Brown 3/30/09

Routing Notes:

Action Adjustment Details

Action Adjustment Step History

Rev #	Entered Step	Entry Date	Step Owner	Step Resp	Exit Date	Exit To Status	User that hit 'GO'	# of Days In Step
1	Request Act Adjustment	3/30/2009	Bonano, Evaristo	Mitcheltree, Brian	3/30/2009	Accept Act Adjustment	Mitcheltree, Brian	0
2	Accept Act Adjustment	3/30/2009	Bonano, Evaristo	Brown, Neil	3/30/2009	Completed	Brown, Neil	0
3	Completed	3/30/2009	N/A	N/A				N/A

Action Adjustment Step History



Condition Report

Record Report

CA Adjustment Report



CR Num	Action Num	Action Adj Num	Step Entry Date	Step	Step Resp	Step Owner
12868	12868-003	12868-003-001	4/28/2009 3:51:32	Completed	N/A	N/A

Action Adjustment Details

Adjustment Number: 12868-003-001

Requested Due Date: 5/19/2009

Date Request Submitted: 4/28/2009

Date Closed: 4/28/2009

Adjustment Title: Due Date Adjustment

Reason for Adjustment:

4/28/09 - B. Mitcheltree - As a result of many RAls from the NRC, the schedule for this CR has suffered.

Adjustment Response:

04/28/2009 Kevin Mon adjustment accepted for Neil Brown

Routing Notes:

Action Adjustment Details

Action Adjustment Step History

Rev #	Entered Step	Entry Date	Step Owner	Step Resp	Exit Date	Exit To Status	User that hit 'GO'	# of Days in Step
1	Request Act Adjustment	4/28/2009	Bonano, Evaristo	Mitcheltree, Brian	4/28/2009	Accept Act Adjustment	Mitcheltree, Brian	0
2	Accept Act Adjustment	4/28/2009	Bonano, Evaristo	Mon, Kevin	4/28/2009	Completed	Mon, Kevin	0
3	Completed	4/28/2009	N/A	N/A				N/A

Action Adjustment Step History

APPARENT CAUSE ANALYSIS FOR CR 12868
"UNEXPECTED TEST RESULTS – RESIDUE ON SUBSET OF ALLOY 22
COUPONS"

Report Date: 11/21/2008
Date Investigation Started: 11/13/2008
Report Number: CR 12868

1. PROBLEM DEFINITION

WHAT: Unknown Residue on Alloy 22 Coupons

WHEN: October 6, 2008

WHERE: Long Term Corrosion Test Facility (LTCTF) at Lawrence Livermore National Laboratory

SIGNIFICANCE:

Safety: No impact to waste isolation

Environmental: No impact

Revenue: No impact

Cost: Cost of Cause Analysis and associated research estimated at \$200,000.00

Frequency: This is a first time event (see Section 8 for additional discussion)

2. BRIEF DESCRIPTION

CR 12868 states the following:

"Inspection of Alloy 22 coupons exposed for 9.5 years in the LTCTF revealed that a subset of the coupons have a visually observable residue on the sample surfaces and adhered to the inside of the plastic bags used for sample storage. While it is possible that the residue is a deliquesced salt, it has a waxy consistency and may be an unexpected organic compound.

Initially, a single sample (DWA158) was identified as having evidence of a residue, and was documented on page 37 of SN-SNL-SCI-046-V3 on 9/22/2008. At the time of the observation the residue on this sample was not considered to be an unexpected test result - the condition of the samples removed from the LTCTF is somewhat variable and DWA158 was initially thought to lie within normal variations. Upon closer inspection of the residue that had been removed and archived during cleaning, it was determined that the substance was not representative of salt deposits that are typically found on coupons removed from the LTCTF.

It was considered due diligence to inspect the remaining uncleaned 9.5 year Alloy 22 coupons. A visual inspection was performed at SNL on 10/06/2008 and 40 out of 132 coupons, primarily from vessels 25 (SAW 60), 26 (SAW 90), and 30 (SDW 90), were identified that may also have some degree of residue. A follow-on inspection of other materials that had been exposed in vessels 25, 26, and 30 was performed at LLNL on 10/15/2008. Uncleaned metal coupons (primarily titanium and Alloys G3, C4, and I825) were visually inspected, and a subset of those samples was identified as possibly having similar residue.

At this time the composition of the residue has not been determined and no trends have yet been identified that clearly indicate the source of the residue.

Therefore, it is not known if the residue is a natural byproduct of the chemical exposure and resulting corrosion processes or if it is a contaminant. An objective of this CR is to ensure that the 9.5 year Alloy 22 coupons having the residue are appropriately identified and tracked such that any influence on the weight-loss measurements and derived corrosion rates can be properly documented. The impact beyond potentially adding uncertainty to the corrosion rates for the 9.5 year Alloy 22 coupons has not been determined."

The apparent cause analysis and testing since CR initiation revealed that the residue on the Alloy 22 samples is an unexpected organic compound, which could have been introduced at different times during the testing and from a multiple of different sources. The cause analysis team concluded based on the available information, the residue precipitated from solution while in the vessels. The source for the residue appears to be either a biofilm, oil/lubricate from stirring motor, or degradation of the vessel and/or sample racks. One action will be planned to prevent reoccurrence and three actions will be planned to further investigate this condition.

3. METHODOLOGY

The methodology used to perform this apparent cause analysis is the Apollo Root Cause Analysis (ARCA) method. The ARCA method is based on fundamental principles, which provide a rule that is applicable to every event-type problem (condition adverse to quality) and is appropriate for Root Cause as well as Apparent Cause Analyses.

The Apollo problem solving process requires that the problem be defined by writing down the What, When, Where, and Significance of the problem. The process starts with the primary effect, the WHAT in the problem definition, and continues by asking "why" or "caused by?" until all answers are exhausted.

Additional methodologies applied include document and training record reviews and survey/interviews with MOWs.

Apparent Cause Analysis Tools

The ARCA method uses RealityCharting v3.2, an electronic tool, to display the answers to the "why" or "caused by?" questions in a useable format for the purpose of recording the causes (as action causes or conditions) that precipitated a Primary Effect. This is called a cause chain and will display the cause boxes as either an action cause or condition (not to be confused with corrective actions or conditions adverse to quality).

The ARCA methodology explains that a cause is either an action cause or a condition cause and requires that each box be identified as one or the other. This categorization assists in determining whether a cause is able to be mitigated by effecting change to an action or an environment. RealityCharting incorporates many internal rules and checks in the process and allows the user to start by defining the problem or by brainstorming causes, to get a handle on what the problem is, until a Stop point (apparent cause) is reached. The user can then apply the appropriate solution (corrective action) to the

Apparent or Root cause(s) that precipitated the Primary Event (condition adverse to quality).

RealityCharting requires that every cause chain end with a purposeful STOP, a GO TO, or have a question mark denoting that a point of inquiry has been reached, which requires additional information to continue to a Stop point. At the Stop point, a possible solution has been identified and can be described as a potential corrective action.

4. CAUSE & EFFECT ANALYSIS

The Causal Analysis team interviewed several individuals that have knowledge of the LTCTF and this CR including:

Neil Brown – LANL/Responsible Manager
Doug Wall - SNL
David Enos -SNL
Kevin Mon – Areva
Gerald Gordon – SNL (consultant)
Kate Helean - SNL
Mark Sutton - LLNL
Jim Blink - LLNL

These individuals were able to provide an insight into the history of the LTCTF and provided information about the current analyses that are directly related to this CR.

The first step in the evaluation of this CR was to identify the composition of the unknown residue on the samples. The residue appeared to be a tan waxy/oil substance through visual inspection. An initial Infrared Analysis (IR) of the residue showed that dominant bands in the spectrum are due to long chain hydrocarbon C-H modes, from methylene (-CH₂-) units. While the spectrum included features due to other IR-active species, the relatively high intensity of these C-H bands indicates that one of the components of the tan material is a simple hydrocarbon of the general formula C_nH_{2n+1}. Such hydrocarbons are the primary component of mineral oils and waxes, whose most common application is as a lubricant. The low intensity bands are due to a carboxylic acid salt, i.e., an ionic compound formed from a neutralized organic acid and a cation, usually of a metal. The IR library provided a number of spectra that reproduced these bands, most of them of calcium stearate (Ca²⁺[n-C₁₇H₃₅COO⁻]₂), which is in the class of compounds that combine long hydrocarbon chains with carboxylic acid groups and are known as “fatty” acids. Because of their long hydrocarbon chains, the spectra of these compounds will also display C-H bands similar to those of simple hydrocarbons, as described in the previous paragraph. However, the low intensity of the carboxylic acid salt bands in the spectrum indicates that it is a minor component that may have been intentionally or inadvertently mixed with the oil/wax described above. Stearate salts are used as plasticizers, stabilizers, soaps, lubricants and waterproofing agents.

Additional LTCTF samples were evaluated to identify any noticeable trends in the quantity of the residue, as to position of sample in the vessel, location on the sample, different solutions/environment and different duration samples. The conclusion was that

the samples appear to have a greater quantity of residue on the bottom side of the samples. The current explanation for this phenomenon is some sort of bubbling action or bubble induced precipitation that accumulated at the bottom of the sample. Also, the samples that were in the vessels for a longer duration tend to have more residue and appear to have a higher percentage with visible residue, for example the 9.5 year samples have more residue present than the 5-year samples. Based on this line of reasoning, the Causal Analysis team assumed that the residue was introduced in the tanks, because if it was introduced afterwards there would not be a preference on where and on which samples the residue accumulated most. The Cause and Effect Chart (Attachment 1) lists the different scenarios that would lead to hydrocarbon introduction to the solutions. It appears that there was a correlation between residue quantity and different solutions/environment, in which the quantity was greater in the SAW and SDW versus the SCW (Attachment 2). There does not seem to be any correlation between position of sample in the vessel and residue quantity. Attachment 3 shows an example of one of the racks that was used in the corrosion testing and the location of some of the samples containing the residue. These conclusions are preliminary and could change with further investigation because all of the samples have not been examined and some have only been visually inspected. Also, there are plans to conduct more IR analyses; these IR and other analyses may give a more definite answer to the composition and hence origin.

The apparent cause was determined using the ARCA method as described above, which is similar to the "why staircase method". The Causal Analysis team evaluated the individual responses from the interviews and facts gathered, and then produced the Apollo Cause and Effect Chart (Attachment 1).

5. APPARENT CAUSES AND RECOMMENDED CORRECTIVE ACTIONS

Based on the Apollo Cause and Effect Chart (Attachment 1), Table 1 identifies the apparent causes and the recommended corrective actions.

The Causal Analysis team came to the conclusion that the potential causes were:

- Biofilm produced the hydrocarbon residue
- The solution degraded the vessel walls and/or racks, causing hydrocarbon in solution.
- Oil/lubricate from stirring motor leaked into solution
- Less than adequate planning, this cause could have prevented the three causes listed above

These four causes are not conclusive by any means, and are currently based primarily on the initial IR analyses already conducted that concluded the residue was a hydrocarbon. Further investigation may reveal that another cause presented on the Cause and Effect Chart (Attachment 1) or an additional cause not identified in this analysis. The team also evaluated human factors involved, which would include accidentally introducing a hydrocarbon residue into the vessels. Considering the hydrocarbon residue can be found in multiple vessels, the same accident would have to occur in all affected vessels. This cause was eliminated due to the low probability of occurring.

In addition to the corrective actions listed in Table 1 to address the causes, the following actions will also be performed:

- 1) Test the residue on the samples more thoroughly to determine if it is consistent with a biofilm (bacteria activity). The additional testing may reveal the origin of the hydrocarbon residue. Action 12868-001
- 2) Confirm the composition of all vessels and racks because the investigation revealed that if the pH was 12 or above, a different type of material was supposed to be used. None of these solution reached that level (10.8 appears to be the highest), but it is possible that the different material was used in the highest pH scenario to provide operational margin. And investigate if there is a correlation between the stirring motors maintenance records and quantities of residue. Action 12868-002
- 3) Compare a population of samples that contains a small amount of the residue to a population of samples that contains a large amount. The comparison is to determine if the calculated corrosion rate (based on measured mass change) of a sample is affected by the presence of the residue. This action will be a key to evaluating the impact of this CR. If it is determined that the residue has no impact on the calculated corrosion rates of the samples, this condition is still an unexpected test result and should be documented to prevent reoccurrence. Then the impact is minimal. If the additional investigations conclude that the corrosion rates are affected by the hydrocarbon residue or if the analysis is inconclusive, then the CR will have to be replanned to revise the appropriate documents, which could include the SAR and TSPA. Action 12868-003

Table 1. Causes and Corrective Actions

CAUSES	CORRECTIVE ACTIONS	ACTION ASSIGNMENTS
Biofilm produced the hydrocarbon residue on the LTCTF samples because the environment was not sterile (Cause Code A4B3)	Document in the Long Term Corrosion Testing Plan to make future corrosion testing environment sterile or devoid of nutrients that would promote biological activity, this could include but not limited to: the use of UV light and additives to the solution. (pending confirmation that it is a biofilm) Action 12868-004	Engineered System Integration Responsible Manager
The solution degraded the vessel walls and or racks, causing hydrocarbon in solution that precipitated on the sample (Cause Code A2B6 and A2B4)	Document in the Long Term Corrosion Testing Plan use of better materials that would not degrade at the temperature, pH, and water chemistry envisioned for each testing environment. Action 12868-004	Engineered System Integration Responsible Manager

The oil/lubricate from stirring motor leaked into tanks. (Cause Code A2B6 and A2B4)	Document in the Long Term Corrosion Testing Plan the prevention of oil/lubricate leaking into the solutions. Action 12868-004	Engineered System Integration Responsible Manager
Less than adequate planning (Cause Code A4B3)	A lesson learned will be added to the Long Term Corrosion Testing Plan to discuss this CR and how the proper planning could have avoided this issue. Action 12868-004	Engineered System Integration Responsible Manager

6. IMMEDIATE/INTERIM ACTION TAKEN

Engineered System Integration Responsible Manager directed all of the staff to refrain from further cleaning of any of the LTCTF samples that may be impacted by the hydrocarbon residue until sufficient information available to proceed without loss of information to close this CR. As for the DTNs that were impacted by this CR, they were already behind the firewall due to actions associated with CR 11851.

7. EXTENT OF CONDITION

The extent of condition is bounded by the samples that were in the LTCTF vessels. The only samples which have been evaluated at this point are the weight-loss and crevice coupons which were made from Alloy 22, Alloy 825, Alloy G3, and Alloy C4. Alloy 22 samples from 5 years were not evaluated as they have already been chemically cleaned. The other coupons in the vessels (U-bend coupons of any composition, or weight loss/crevice coupons made from Ti Grade 12, Ti Grade 16, and 625) have not yet been evaluated (so it is unknown at this point if any of them have a similar residue).

8. PREVIOUS OCCURRENCES

A thorough search of the CAP system returned three CRs that were owned by the Lead Lab that could be linked to LTCTF samples:

1) CR 11851: Unexpected Cleaning Weight Loss of Alloy 22 Control Samples

This open CR is for unexpected test results for weight loss that occurred during a scoping test activity on Alloy-22 control samples. There are on-going activities for this CR. However, several remedial actions have already been taken. The technical procedure for cleaning the samples has been replaced with the procedure TST-PRO-T-008 due to the CR, which requires that all samples (or a documented portion of samples) are cleaned until there is no significant weight loss between cleaning cycles. A Lessons Learned document has been incorporated in the Long-Term Corrosion Testing Plan SAND2007-7027. Also, for the 5-year Alloy 22 corrosion coupons a comparison of the 2008 current weight versus 2002 clean weight has been completed.

2) CR 5421: Identification of specific storage location for specimens.

This closed CR is a level D, and was a suggestion for improvement of the storage of samples at the LTCTF. The suggestions involved an enhancement in Access Database maintained by the PI for the LTCTF samples and also placing check-out cards for the storage cabinets. The resolution was to add the check-out cards and to add more details to the Access database and this has been completed. There was no deficiency on the storage of the samples noted in this CR, there were only suggested improvements to be made.

3) CR 11919: Errors Regarding Certain Corrosion Testing Solutions

Contrary to the requirements of IM-PRO-003 (Software Management), unqualified software (Geochemist's Workbench v. 2.0) was used in DTN: LL040803112251.117 to compute simulations of the evaporation of "representative" Yucca Mountain groundwater to obtain the target compositions of the corrosion testing solutions SDW (Simulated Dilute Water) and SCW (Simulated Concentrated Water). The conclusion from this CR was to use the measured compositions not the target compositions. This CR is still pending on revisions to corrosion documents and the SAR.

Previous Occurrence Summary: In review of these three CRs, none identified a condition similar to the condition identified in CR 12868. As such, these actions would not have prevented this occurrence.

9. EFFECTIVENESS REVIEW PLAN

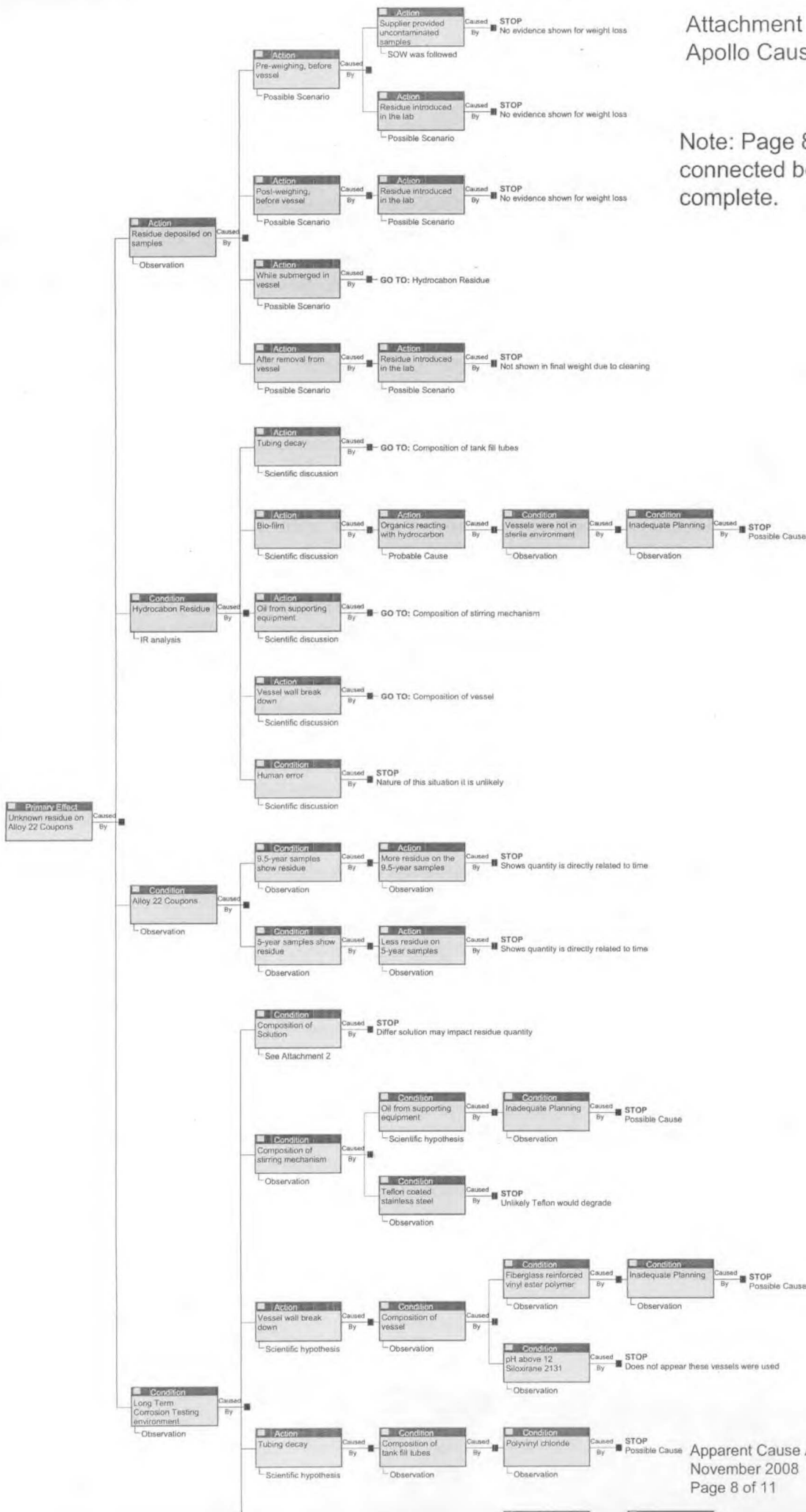
Because the LTCTF has been shut down there would be no way to evaluate the corrective actions presented in this apparent cause analysis for effectiveness.

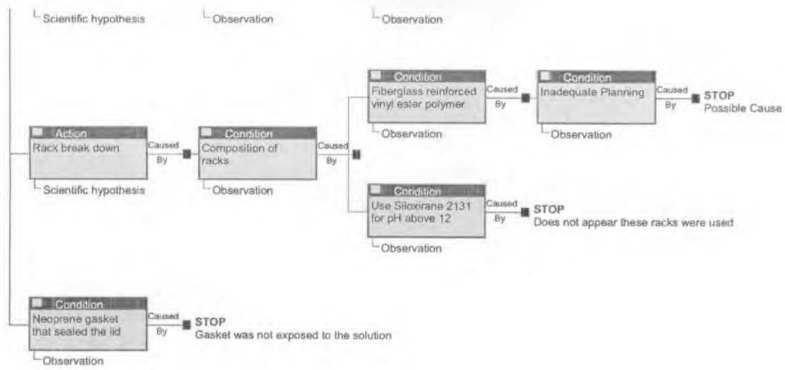
10. INVESTIGATION TEAM MEMBERS:

Cause Analysis Lead: Brian Mitcheltree
QCS Participants: Peter Persoff, Michael Russell
Participants: Jeff Gromny

Attachment 1. Apollo Cause and Effect Chart

Note: Page 8 and 9 need to be connected bottom to top to be complete.





Attachment 2: Relevant LTCTF Test Solution Compositions

Ion		SDW (mg/L)	SCW (mg/L)	SAW (mg/L)
K ⁺	Minimum	3.58×10^1	1.35×10^3	3.25×10^3
	Average	3.69×10^1	3.48×10^3	3.51×10^3
	Maximum	3.94×10^1	4.96×10^3	3.86×10^3
Na ⁺	Minimum	3.30×10^2	3.36×10^4	3.92×10^4
	Average	4.10×10^2	3.99×10^4	4.22×10^4
	Maximum	4.68×10^2	4.36×10^4	4.36×10^4
Mg ²⁺	Minimum	0.00	0.00	4.99×10^1
	Average	6.62	5.68×10^{-2}	5.31×10^1
	Maximum	2.75×10^1	2.35×10^{-1}	5.72×10^1
Ca ²⁺	Minimum	0.00	1.11	4.95×10^1
	Average	1.29×10^1	1.90	6.73×10^1
	Maximum	4.51×10^1	2.74	9.65×10^1
F ⁻	Minimum	0.00	1.03×10^3	0.00
	Average	9.39	1.26×10^3	2.68×10^2
	Maximum	3.02×10^1	1.48×10^3	7.75×10^2
Cl ⁻	Minimum	5.83×10^1	5.42×10^3	2.21×10^4
	Average	1.12×10^2	6.47×10^3	2.25×10^4
	Maximum	1.36×10^2	7.56×10^3	2.77×10^4
NO ₃ ⁻	Minimum	4.04×10^1	6.04×10^3	2.37×10^4
	Average	2.23×10^2	6.77×10^3	2.47×10^4
	Maximum	7.54×10^2	7.45×10^3	2.53×10^4
SO ₄ ²⁻	Minimum	1.55×10^2	1.21×10^4	4.35×10^4
	Average	2.32×10^2	1.52×10^4	6.00×10^4
	Maximum	2.96×10^2	1.92×10^4	6.95×10^4
HCO ₃ ⁻	Minimum	1.10×10^1	1.18×10^4	0.00
	Average	2.09×10^2	2.95×10^4	3.06×10^{-1}
	Maximum	5.39×10^2	4.28×10^4	9.51×10^{-1}
Si	Minimum	0.00	1.60×10^1	2.60×10^1
	Average	6.52	4.39×10^1	4.52×10^1
	Maximum	2.21×10^1	1.07×10^2	6.77×10^1
pH	Minimum	8.37	10.14	2.77
	Average	9.48	10.44	3.33
	Maximum	10.15	10.76	3.88

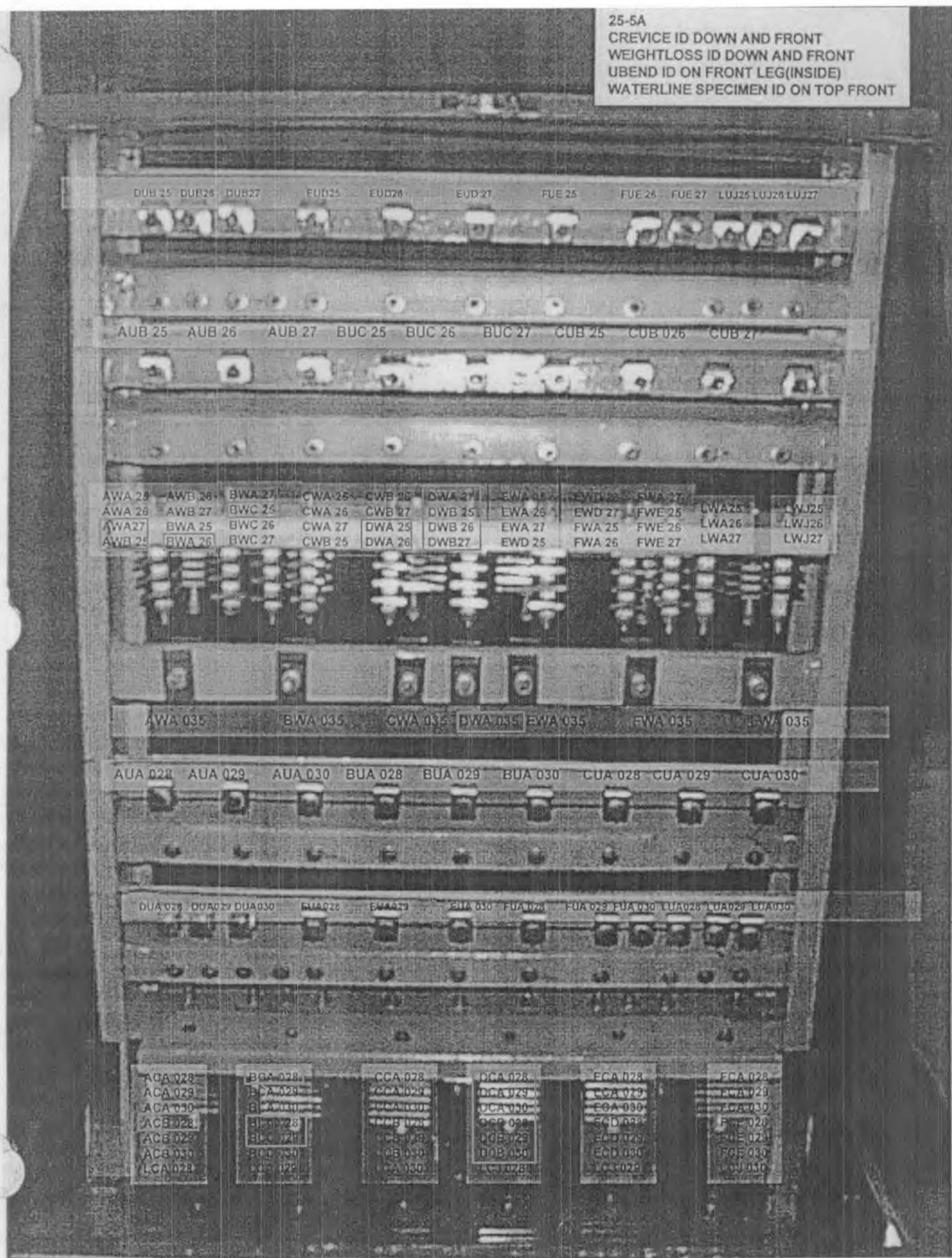
Source: DTN: LL081002312251.202 [DIRS 185793], file:
Revised_Vessel_Chem_02and04v4.xls, worksheet: Range (Note: pH measured for the
actual solution at room temperature)

SCW- simulated concentrated water

SDW- simulated dilute water

SAW- simulated acidic concentrated water

Attachment 3. Photograph of racks with coupons before inserted into the vessel (red boxes indicate samples with residue)

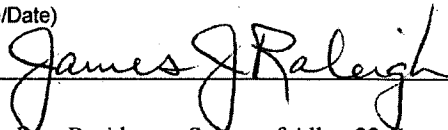


Reportability Determination for CR 12868

Section 1 – Initiator Notification of Information Potentially Reportable Under: 10 CFR 21 and 10 CFR 63

Initiator: (Print/Signature/Date)

James J. Raleigh /



/ 12/19/08

Condition Report (CR) No.:

CR 12868

Title:

Unexpected Test Results – Residue on Subset of Alloy 22 Coupons

Brief Description:

CR 12868, Condition Description, identified that the inspection of Alloy 22 coupons exposed for 9.5 years in the Long Term Corrosion Testing Facility (LTCTF) revealed that a subset of the coupons had a visually observable residue on the sample surfaces and adhered to the inside of the plastic bags used for sample storage. The residue has been determined to be organic in nature. The condition was considered to have a potential impact on the weight-loss measurements conducted on the samples and the derived corrosion rates as relied upon in the License Application (LA). However, it is important to note that the LA does not, at this time, discuss nor does it rely on the 9.5-year sample data.

The preliminary impact analysis, as documented in Initial Technical Work Activity Evaluation IAE-08-0038, has concluded that the existence of the hydrocarbon (organic) residue is unlikely to affect corrosion rates as the oxygen permeability needed to support low corrosion rates is extremely low. Testing will be performed in March and April of 2009 to compare corrosion rates between relatively clean samples and dirty samples to determine if there is a discernable difference.

Reporting pursuant to 10 CFR 63.10(b) is required when information provided to the NRC is incomplete or inaccurate AND has, for the regulated activity, a significant implication for public health and safety or the common defense and security of the United States. To date, discussion of the 9.5-year sample data is not contained in licensing basis as described in the LA. As such, reportability in accordance with 10 CFR 63.10 on this new information is not applicable. The evaluation of this condition has determined that the potential impact on the corrosion rate presented in the LA (based primarily on 5-year corrosion test data) will not present a "significant implication" related to safety. Thus, the identified condition does not satisfy these reporting criteria and, therefore, is not reportable in accordance with 10 CFR 63.10.

Reporting pursuant to 10 CFR 63.73 is required when a deficiency is found in the characteristics of the Yucca Mountain site, and design, and construction of the geological repository operations area (GROA) that, were it to remain uncorrected, could (1) adversely affect safety at any future time; (2) represent a significant deviation from the design criteria and design basis stated in the design application; or (3) represent a deviation from the conditions stated in the terms of a construction authorization or the license, including license specifications. This testing finding does not satisfy these reporting criteria. For completeness, the remaining subparts of 10 CFR 63.73 are not applicable at this time.

Reporting pursuant to 10 CFR 21 is not required as this condition does not involve a defect of an item procured as a basic component.

Personnel Notified: (Name of DOE RAO Person)

Neal Hunemuller



Notification Time and Date:

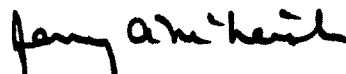
1426-Hours, 12/19/08

Section 2 – DOE Contractor Licensing Manager Review and Recommendation to DOE RAO

Review and Recommendation:

Name: (Print/Signature/Date)

JERRY McNEISH



12.23.08

Scientist *WKA*, 12/23/08

Section 3 – DOE Director, Office of the Chief Engineer Review and Recommendation to DOE RAO

Review and Recommendation:

Recommend that the results of testing to be performed in March and April be evaluated and any reportable condition made known to NRC per requirements.

Name: (Print/Signature/Date)

*Susan Jones for J.R. Dyer *[Signature]* 12/23/08*

Section 4 – DOE RAO Review and Final Decision on Reportability of Information per:

Is information reportable per: *10CFR63.10, .73, 10CFR21* ☐ Yes ☒ No

DOE RAO Name: (Print/Signature/Date/Time)

WILLIAM BOYLE for April Gil APRIL GIL 12/23/08 1500hU.

Section 5 – Closure

Date DOE RAO notified: _____ Date: _____ Receiver Name: _____ Method: _____

DOE RAO Name: (Print/Signature/Date/Time)

Section 6 – Records Retention

Provide this completed form to the Corrective Action Program Manager (or designee) so it can be attached/included as part of the CR cited within Section 1.

CR Closure Verification Checklist

Personal or sensitive information should not be included in condition reports.

Documentation should provide traceable, verifiable, objective evidence that will demonstrate that each action was completed as stated in the plan within the CR record. It should be in sufficient detail that uninvolved third-party reviewers can understand the reasons behind the decisions made, analysis, extent of condition, and corrective actions.

CR Number: 12868 CR Level: B Resp. Org: SNL Conducted by: Wendy Mitcheltree

Attribute	Applicable To Level(s)	Yes/No NA	Comments
Miscellaneous CR Fields			
If Involve Initiator field is "Yes," does the <i>Disc Plan w/Init</i> and/or the <i>Disc Impl w/Init</i> field have appropriate wording to affirm?	A-D	YES	Called & talked to initiator. He was fine with the resolution and was involved in many steps of the resolution.
If the <i>LL/GI Required</i> field is "Yes," has a lessons learned been submitted?		YES	LL was submitted via the testing plan in Action004.
CAQs			
<i>Requirement Involved</i> is "Yes"	A-C	YES	
If the <i>Requirement Involved</i> field is "Yes," is the <i>Requirement</i> field completed with something other than TBD?		YES	
Trend Only, if applicable			
Does CR clearly state what was corrected and/or why no further action is required	C-D	N/A	
Extent of Condition (EoC)			
Is documented in the CR	A-B	YES	It is located in the cause analysis report attached to this CR.
The bounding methodology is appropriate and documented in the CR		YES	
Apparent or Root Cause			
Is clearly stated	A-B	YES	It is located in the cause analysis report attached to this CR
Identified Cause(s) are supported by investigative findings		YES	List is in the cause analysis.

Attribute	Applicable To Level(s)	Yes/No NA	Comments
<u>Previous Occurrence</u>			
Is documented in the CR	A-B	YES	It is located in the cause analysis report attached to this CR.
Identified similar CRs		YES	List is in the cause analysis.
<u>Corrective Actions</u>			
Identify Actions to preclude recurrence	A	N/A	
Address the Cause(s) identified or there was adequate explanation of why no action was necessary	A-B	YES	
Is clear enough to identify that the corrective action(s) was completed satisfactorily	A-D	YES	
Support the correction of the condition identified in the CR		YES	
If actions were not completed as stated, an explanation was provided		YES	
If no action will be taken, rationale is provided		YES	
<u>Documentation</u>			
Additional documentation, as referenced, has been attached or its location has been identified	A-D	YES	
<u>Closing one CR to an existing CR, if applicable</u>			
The issue documented within the new CR is already addressed within the existing CR	A-D	N/A	
The newer CR is closed to an older CR		N/A	
The higher significance level CRs is not closing to a lower significance level CR		N/A	
<u>Closing to another Business Process, if applicable</u>			
The business process(es) is a controlled process, managed by procedure, periodically assessed, and tracked/trended.	D	N/A	
When utilizing other business processes to track the completion of the action(s):		N/A	
1) There is a clear statement documents the process that will be utilized to track action(s),		N/A	
2) There is a cross-reference to a tracking number(s) within that process, and		N/A	
3) There is a clear statement how the process is documented and periodically assessed		N/A	

Attribute	Applicable To Level(s)	Yes/No NA	Comments
Non-Valid CR, if applicable			
Documentation clearly affirms that the original issue was not valid	N/A	N/A	

Analysis of organic deposit on Alloy 22 coupons

Summary:

GPC and NMR analysis were employed to assist in the characterization of an unknown material appearing to be of organic nature, deposited as a thin film on Alloy 22 coupons. Both ^1H and ^{13}C NMR suggest the organic component to be mainly hydrocarbon based with some unsaturation, but little evidence of oxidized carbons. Further, there is no evidence for nitrogens bonded to carbon ruling out a bio-film (protein containing deposit). GPC molecular weight (MW) analysis establishes the presence of a broader distribution of oligomeric components within an approximate range of MW 1000 to 5000 g/mol. The organic material most likely originates from a lubricant, grease or similar source. It is likely not a compound that would have been extracted from any commercial polymers, as the identified molecular weight range is too high for common additives and leachable materials to be involved. However, metal based components, polymeric parts or similar, with processing aids or grease on their surface could qualify as a source. Likewise, it is also feasible that organic oil components could have served as a source and increased in their molecular weight with time, as hydrocarbon based oils commonly contain reactive unsaturation and could build up gum.

Problem:

A thin film residue that appeared to be of organic nature was found on Alloy 22 coupons exposed to corrosive water based salt solutions for long term aging studies. The exact source and type of the deposited material is unknown. To provide guidance on the nature and potential origin of the deposited film, strategies for analysis were discussed. An IR spectroscopic screening suggested a hydrocarbon based material with potentially carboxylate and saponification features. During a follow-up discussion it was decided to pursue NMR spectroscopy for better chemical information and GPC analysis to provide guidance on the molecular weight of the material.

Methods applied:

For further analysis of the material we employed GPC and NMR. Gel permeation chromatography (GPC) can identify the approximate molecular weight and separate any high and low molecular weight compounds. It is suitable for small samples, less than 1mg/ml are required. NMR spectroscopy was applied in both ^1H (< 1mg/ml) and ^{13}C (ideally a few milligrams) analysis. NMR spectra provide guidance on both the chemical nature of the molecular building blocks and their relative ratios, ie. percentage of oxygenated carbons versus aliphatic, or any silicone carbons. Coupled with some knowledge of MW, simple organic molecules can be easily narrowed-down or identified.

GPC analysis:

GPC analysis was conducted using columns optimized to the separation of lower molecular weight materials and oligomers. Since polymer additives potentially picked up from syringes or any similar lab items may mimic organic contamination, great care was taken to assure to the highest degree possible that the GPC result are specific to the YM sample material supplied to us. Analysis was conducted by GPC analysis of:

- a) a THF pure solvent (tetrahydro furan) sample,
- b) a blank sample that did not contain the unknown YM material, but contained the same amount of THF solvent, was held in the same ampoule for the same amount of time and was exposed to the same sample handling and solvent filtration process,
- c) the YM sample dissolved in THF, prepared, filtered and readied for GPC analysis.

Sample preparation: Samples were prepared twofold, one as a sample containing the unknown material and a second one as a blank, just the solvent with all the identical processing and handling. The unknown material scraped off as the deposit from the alloy test plaques was used as provided. 13.4 mg was placed in a ~2ml vial. Using a new 1ml syringe 0.5 ml pre-filtered THF was added. The sample was then dissolved by shaking the vial for about 1 min. The solution in the sample containing vial turned slightly opaque and brownish. The sample was then allowed to have most of the inorganic micro-crystalline material (salts insoluble in THF) settle at the bottom for about 30 minutes. A new syringe was used to pick up ~ 0.25 ml from the top of the solution and then filtered through a 0.2 micron sized PTFE filter element. A few filtered droplets were obtained in a new sample vial and used for injection into the GPC.

System: Agilent 1100 with refractive index and UV detector.

Column temperature: 40°C.

Columns: Two columns in series, a PLgel 5 μ m 100A (MW: 100-4000 g/mol) followed by a PLgel 5 μ m 50A (MW: 0-1000 g/mol).

Solvent: HPLC grade pure THF.

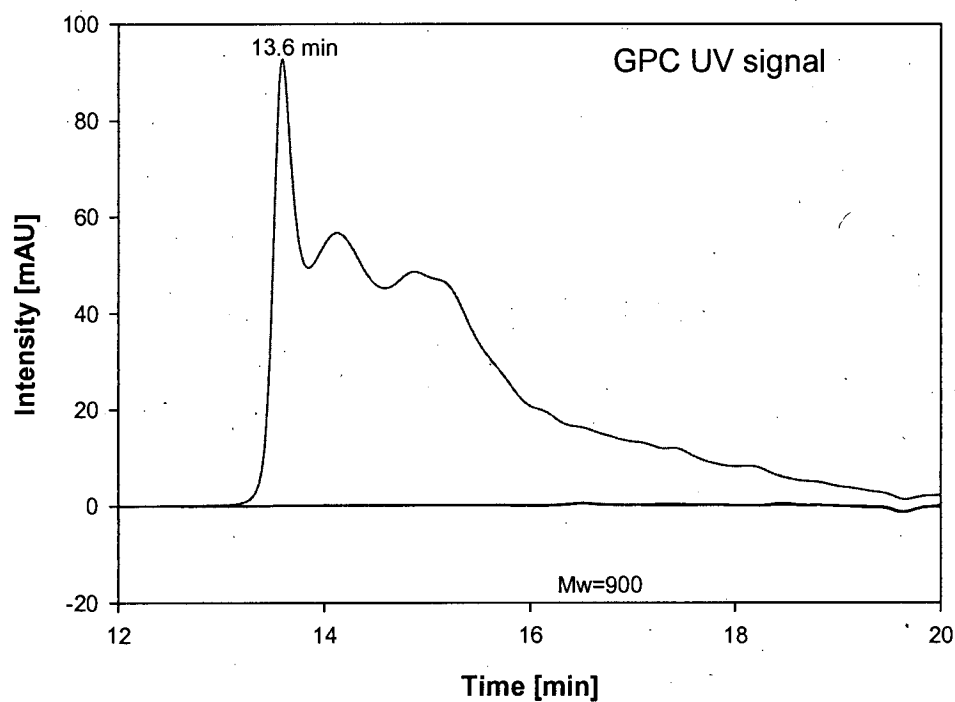
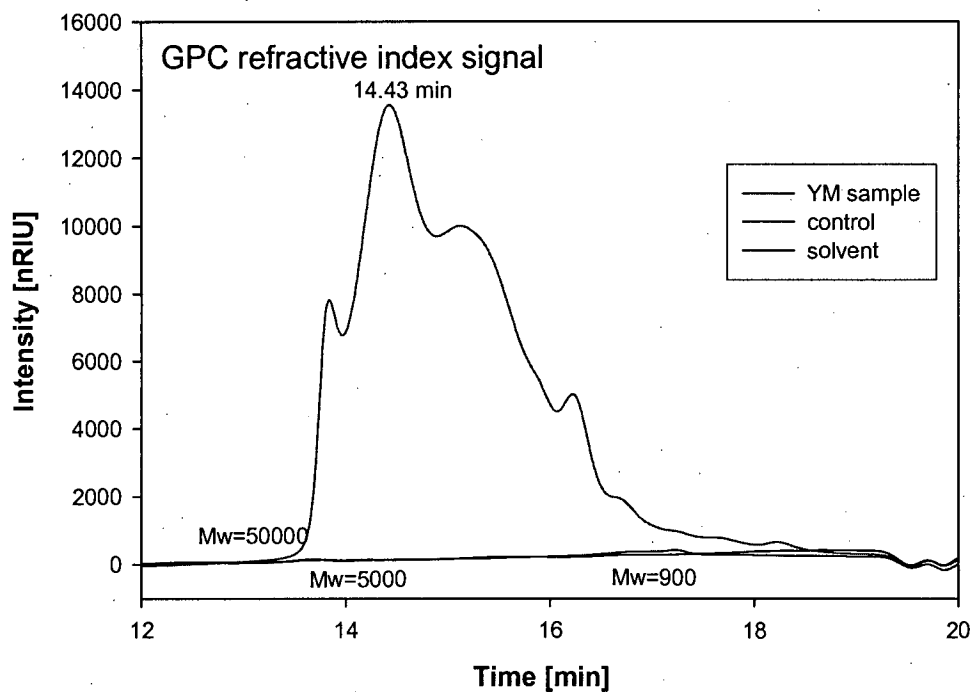
Flow rate: 0.75 ml/min.

Injection volume: 20 micro liters.

GPC traces and results:

There is a non-linear relationship between molecular weight and elution time. For the RID detector, 16 min elution time equates to approximately MW of 900 g/mol (based on a BMI reference material), and from polybutadiene standards, 14 min equals MW ~5000 g/mol, and 13.5 min is MW ~50000 g/mol. The UV detector signal is approximately 0.25 minutes earlier for similar molecular weights. Based on the timing of the detector responses and in comparison with polybutadiene standards, the unknown sample contains oligomers in a molecular weight range of ~1000 to 5000 g/mol (70-360 -CH₂ groups). There is also a noticeable difference between the traces depending on the detector. This means that some sample constituents have higher UV absorbance than others and vice versa. For example, a higher molecular weight component at 13.6 min has considerably higher absorbance suggesting the presence of more ketones, conjugated unsaturation or

similar structures. It means there is some variability in the specific type of chemical make-up as a function of molecular weight. Also, since UV absorbing molecules were detected, they are not simple saturated hydrocarbons and must contain at minimum some UV absorbing functional groups.



GPC analysis of filtered organic material dissolved in THF using two detectors, refractive index and UV. Elution time provides guidance on molecular weight.

NMR analysis report:

Sample: ^1H and ^{13}C NMR
Operator: Todd M. Alam, Org 1816 MS 0886
Data: Alam XII / diff_setup_111708 (avance 600)
Date: 11/19/08, 11/24/08
Report Date: 11/25/08
Contact: Mat Celina
Filename: Celina_112508.doc

Description:

^1H and ^{13}C solution NMR of unknown material designated as YM_1 dissolved in THF- d_8 .

Experimental:

The high resolution ^1H and ^{13}C NMR spectra were obtained on a Bruker DRX400 at 399.87 and 100.54 MHz, respectively, using a 5 mm broadband probe, at 25 oC using standard pulse sequences. The chemical shifts were all referenced to internal TMS present within the THF- d_8 solvent.

Discussion:

^1H NMR

The ^1H NMR spectrum for the YM_1 sample is shown in Figure 1. The resonances from the THF- d_8 residual solvent peaks, HDO and TMS are noted. The ^1H NMR spectrum of the unknown is dominated by the CH_2 resonance at $\delta = 1.2$ ppm (relative integral 81.5%), and the CH_3 resonance at $\delta = 0.8$ ppm (17.5%). These are consistent with the assignment to a long chain alkane (see ^{13}C discussion). There is also a minor set of vinyl resonances (total concentration $\sim 1\%$) located between $\delta = 7$ and 6.5 ppm. This large discrepancy in relative amounts suggest that this material is not a single compound, but a mixture of different species, including alkane chains with a small amount of vinyl functionality.

^{13}C NMR

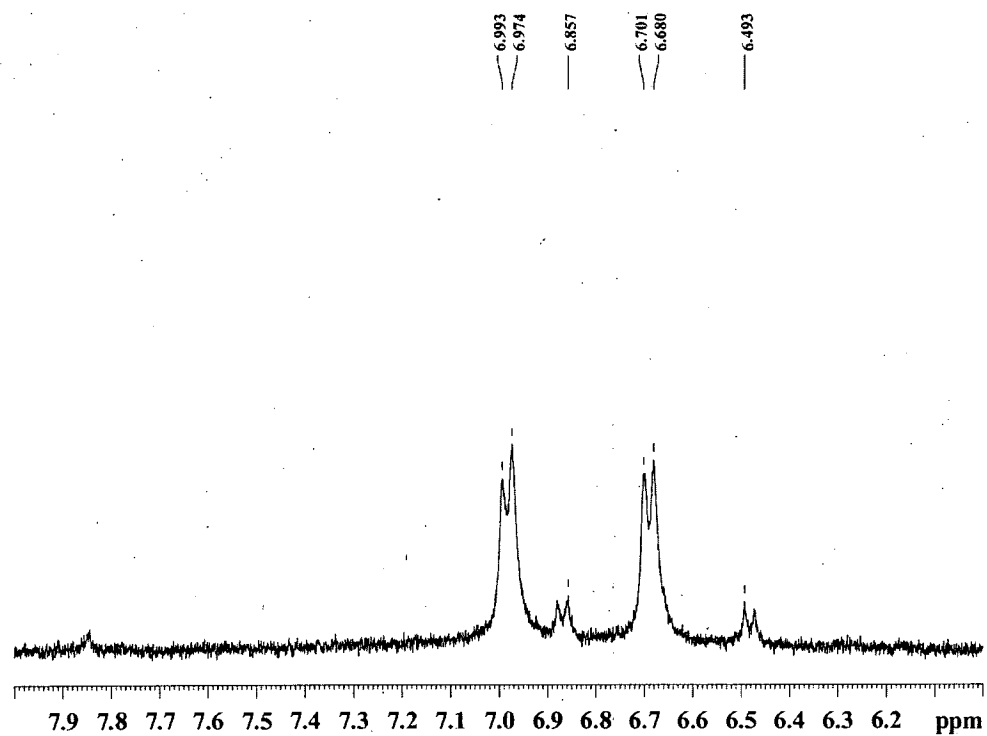
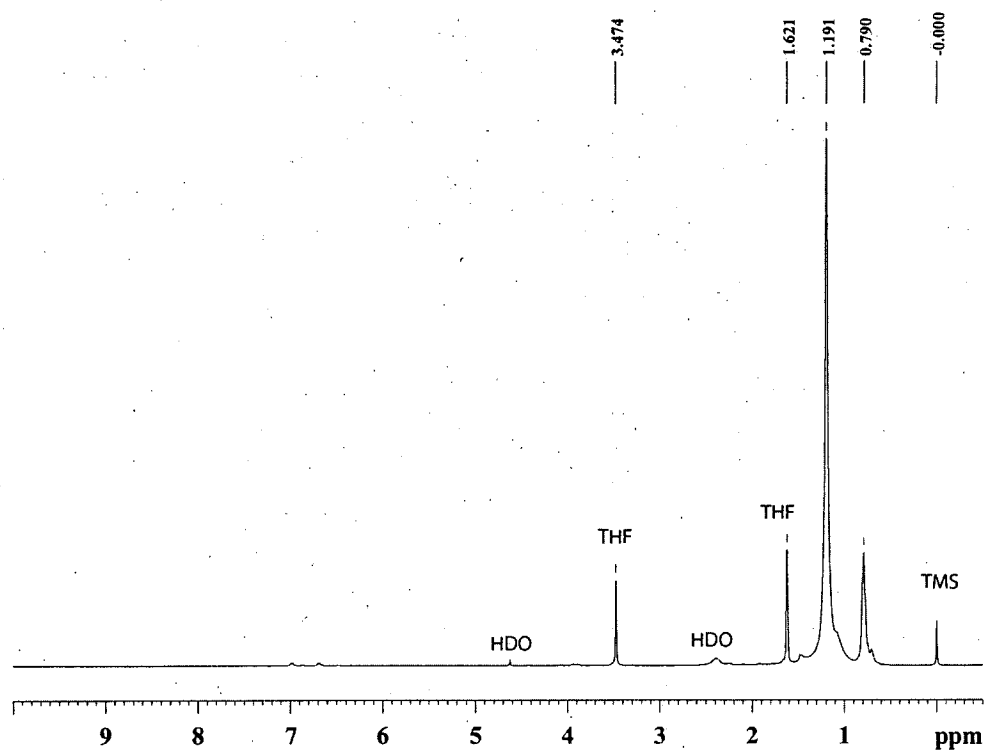
The ^{13}C NMR spectrum is shown in Figure 2. The signals from the THF- d_8 are dominant ($\delta = 66.0$ and 24.0), but multiple signals from the unknown are observed. An INEPT NMR spectrum allowed the multiplicity of these carbons to be determined (CH , CH_2 and CH_3). These results are summarized below.

Major ¹³ C Resonances (ppm)	Multiplicity	
31.5	CH ₂	Alkane
29.7	CH ₂	In chain alkane
29.0	CH ₂	In chain alkane
22.2	CH ₂	Alkane
13.1	CH ₃	Methyl – alkane
Minor ¹³C Resonances (ppm)		
127.0	CH	Vinyl – double bond
113.3	CH	Vinyl – double bond
41.7	CH ₂	
39.2	CH	
37 – 33 (multiple weak resonances)	CH	
30.3	CH ₂	

*Note – there are no ether (C-O-C) type carbon linkages as these would appear between 45 and 70 ppm.

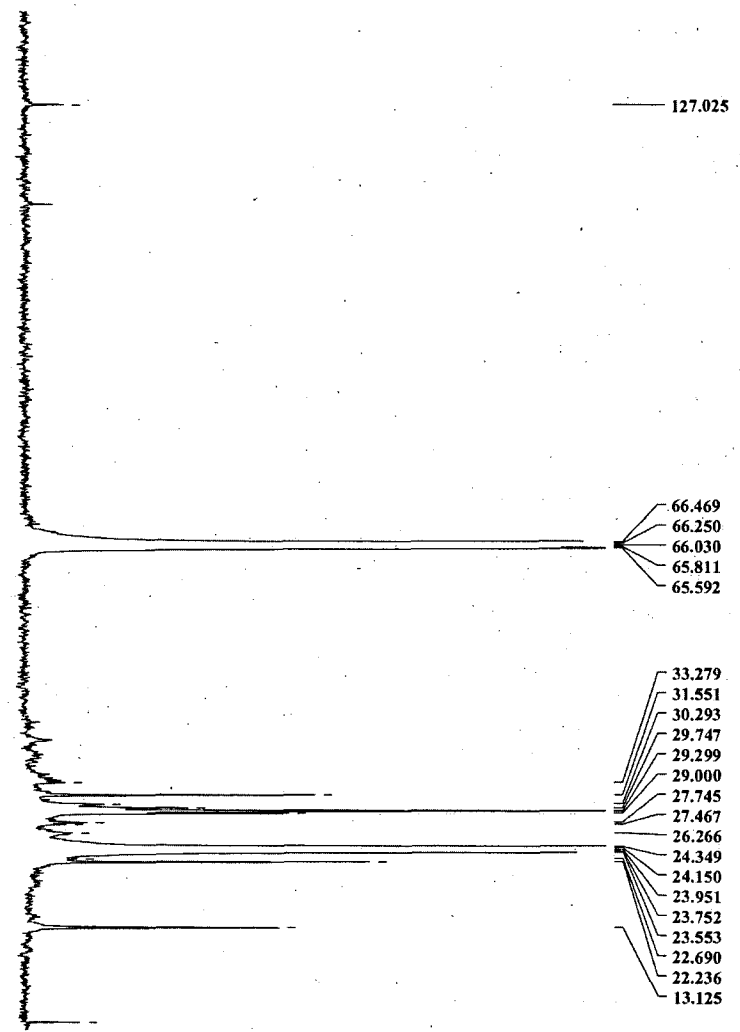
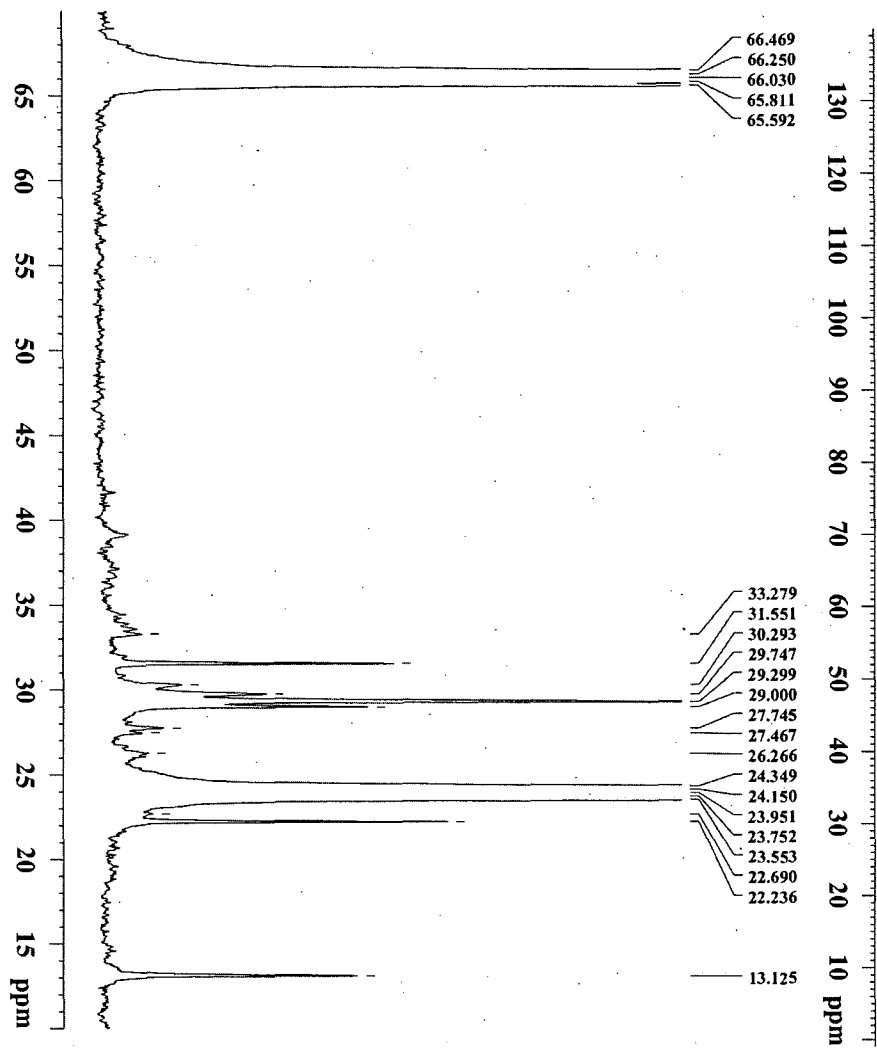
**Note – No carbonyl or aldehyde resonances were observed.

The large difference in intensities between the major and minor resonances suggests that this is a mixture of different organic species. A library search of the major resonances (NMRShiftDB) gives the highest match level to a range of different alkane chain compounds. Addition of the 2 resonances at 127 and 113.3 ppm provides target hits for long chain alkanes with a terminal vinyl species.



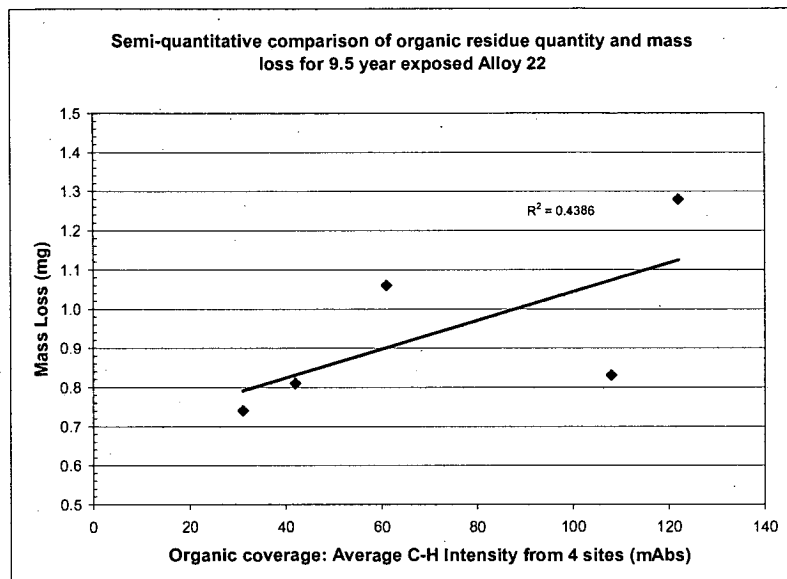
^1H spectrum

^{13}C spectrum



Sample ID	Highest C-H Intensity	Average C-H Intensity -- mAbs	Mass Loss (pre-test weight - post clean weight) -- mg	Corrosion rate nm/yr
DWA100	43	31	0.74	2.9
DWA098	82	42	0.81	3.2
DWB100	105	61	1.06	4.3
DWB099	318	108	0.83	3.4
DWB098	368	122	1.28	5.2

Average C-H Intensity -- mAbs	Corrosion Rate nm/yr
31	2.9
42	3.2
61	4.3
108	3.4
122	5.2



Using the regression tool from the Data Analysis Toolpack:
SUMMARY OUTPUT

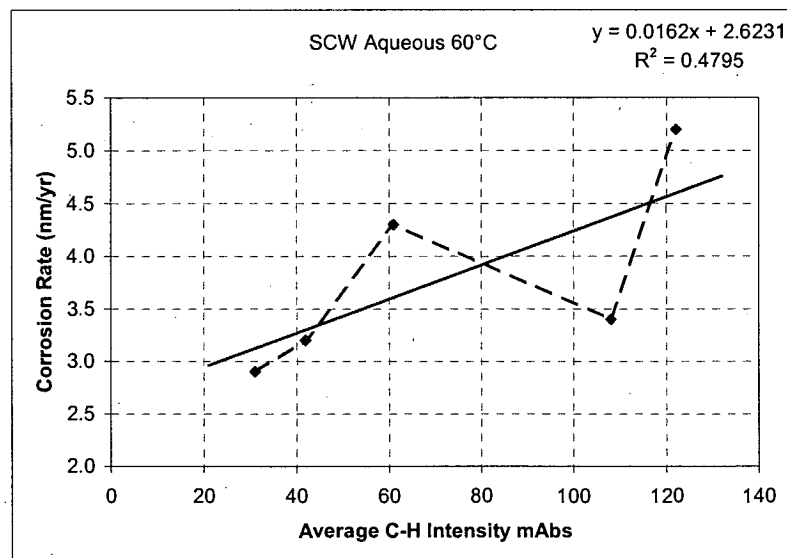
Regression Statistics	
Multiple R	0.692476081
R Square	0.479523123
Adjusted R Square	0.306030831
Standard Error	0.783685342
Observations	5

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	1.697511856	1.697511856	2.763944822	0.194996793
Residual	3	1.842488144	0.614162715		
Total	4	3.54			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	2.623058447	0.789934925	3.320800677	0.045033883	0.109132963	5.13698393
Average C-H Intensity -- mAbs	0.01616678	0.009724311	1.662511601	0.194996793	-0.014780318	0.047113877

Ho Slope = 0
Ha Slope not = 0

The P-value for the slope term "Average C-H-Intensity -- mAbs" and equivalently the Significance F indicate that there is almost a 20% chance that randomly obtained data would fit the linear equation as well as the data analyzed. Thus, it can be concluded that there is no significant correlation between Corrosion Rate and Average C-H-Intensity -- mAbs.



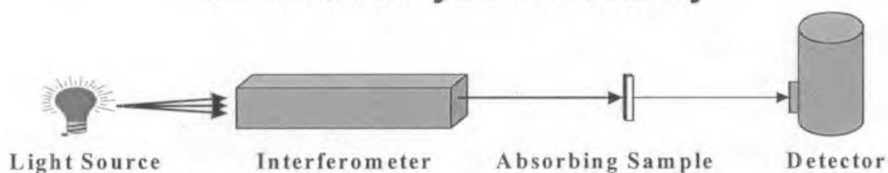


Sandia National Laboratories

Operated for the U.S. Department of Energy by
Sandia Corporation
Albuquerque, New Mexico 87185-1411

Analysis Report

Infrared Analysis Laboratory



Infrared Spectrum

Date job accepted: 10/22/08

Job Number: FTIR09007

File Name: FTIR09007.doc

Program: Yucca Mountain Project

Description: Analysis of unknown material

Project/task: 100837/10.03.05.15
134772/10.03.05.15 (do not include on any copy of the report which is transmitted outside of SNL)

Requester Info

Name	Org.	Phone		MS
		Voice	FAX	
Doug Wall	1823	844-6904		0888

Sample List

Sample #	Description	Date		Picked up	Returned
		Picked up	Returned	By	To
1	Cotton swab with tan colored material (picked up from Ted Borek)	10/21/08		B. Montoya	
	Alloy 22 coupons DCB155, DWA097, DWA158 and DWB025; plus cleaned alloy 22 coupon DCA288, which was used to provide the background spectrum to which the spectra of the others were ratioed.	11/3-5/08	11/3-5/08	In custody of E. Lopez	
	Alloy 22 coupons DCB089, DWA099, DCA120 and DWA138; plus cleaned alloy 22 coupon DCB200, which was used to provide the background spectrum to which the spectra of the others were ratioed.	11/18/08	11/18/08	In custody of Kate Helean	
	Alloy 22 coupons: Reference Coupon DCA288 and cleaned coupons ACA156 and BCC155	1/15/09	1/15/09	In custody of E. Lopez	
	Alloy 22 coupons: Reference Coupon DCB200 and coupons DWA098, DWA100, DWB098, DWB099 & DWB100, all with "60°C" notation	2/23/09	2/24/09	In custody of E. Lopez	

Background Information and Work to be Performed

Survey the coupons using infrared (IR) spectroscopy and identify deposits on their surface.

Preliminary Report

date: 10/27/08

to: Doug Wall

via: DVD-in-person

We removed small pieces of the tan material from the swab and placed them between salt windows for infrared (IR) analysis in transmission mode using a Fourier transform spectrometer and an IR microscope. A representative spectrum from the tan material is shown in Figure 1. The consistency of the tan material is that of a wax or a very viscous oil.

The dominant bands in the spectrum shown in Figure 1 are due to long chain hydrocarbon C-H modes, from methylene ($-\text{CH}_2-$) units. While the spectrum includes features due to other IR-active species, the relatively high intensity of these C-H bands indicates that one of the components of the tan material is a simple hydrocarbon of the general formula $\text{C}_n\text{H}_{2n+1}$. Such hydrocarbons are the primary component of mineral oils and waxes, whose most common application is as lubricants. See the comparison to a library spectrum in Figure 2.

The bands in the 1500 cm^{-1} to 1700 cm^{-1} are due to a carboxylic acid salt, i.e., an ionic compound formed from a neutralized organic acid and a cation, usually of a metal. Our IR library provided a number of spectra that reproduced these bands, most of them of calcium

stearate ($\text{Ca}^{2+}[\text{n-C}_{17}\text{H}_{35}\text{COO}]_2$), which is in the class of compounds that combine long hydrocarbon chains with carboxylic acid groups and are known as "fatty" acids. Because of their long hydrocarbon chains, the spectra of these compounds will also display C-H bands similar to those of simple hydrocarbons, as described in the previous paragraph. However, the low intensity of the carboxylic acid salt bands in the spectrum of Figure 1 indicates that it is a minor component that may have been intentionally or inadvertently mixed with the oil/wax described above. Stearate salts are used as plasticizers, stabilizers, soaps, lubricants and waterproofing agents. See the comparison to a library spectrum in Figure 3.

The band labeled Si-O in Figure 1 does not appear to be associated with the hydrocarbon and carboxylic acid salts. It is probably a silicate mineral present in the dust/dirt/sand particles visible in the sample.

The sample is composed primarily of a hydrocarbon oil/wax, plus a carboxylic acid salt similar to calcium stearate and silicate-based dust/dirt/sand particles.

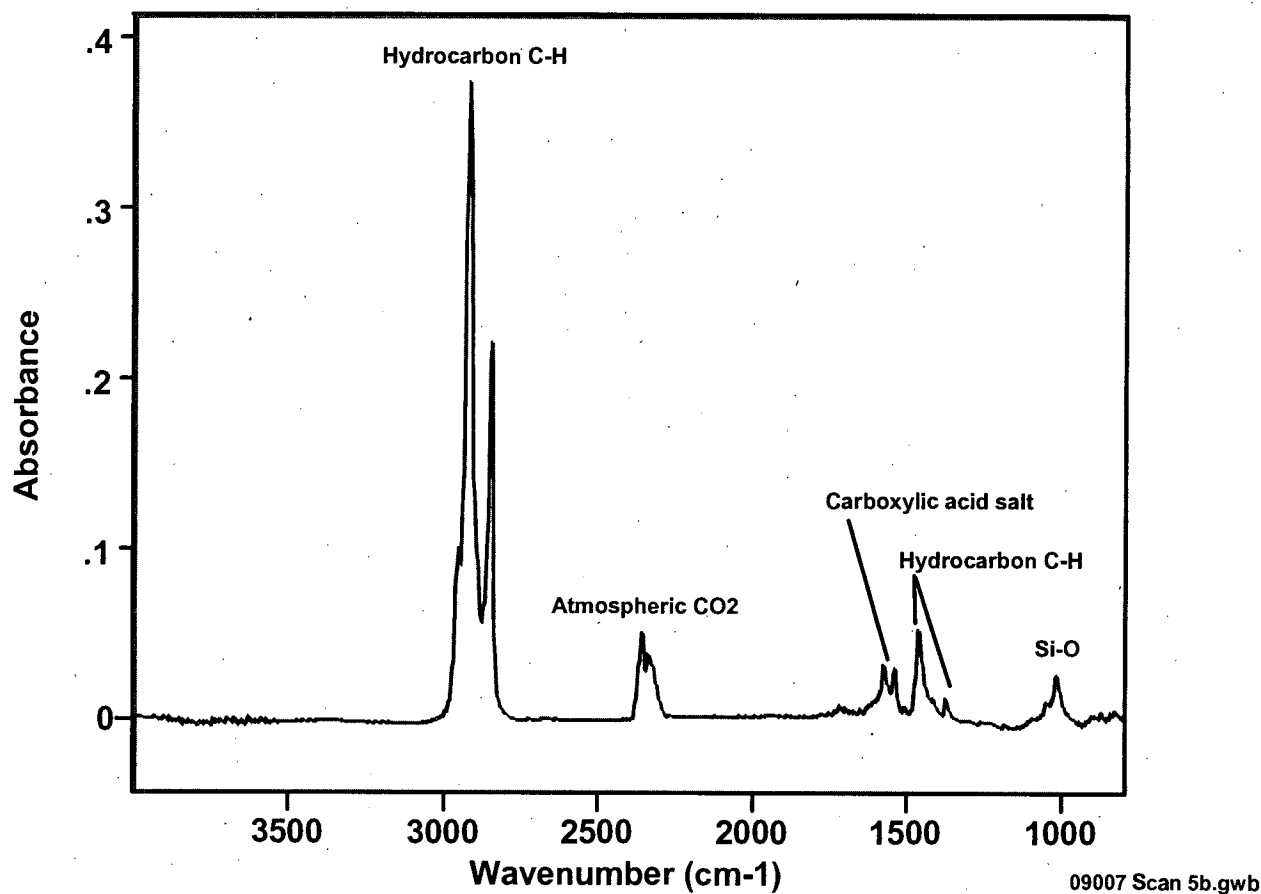


Figure 1. Micro-transmission IR spectrum of tan-colored material on swab (YMP)

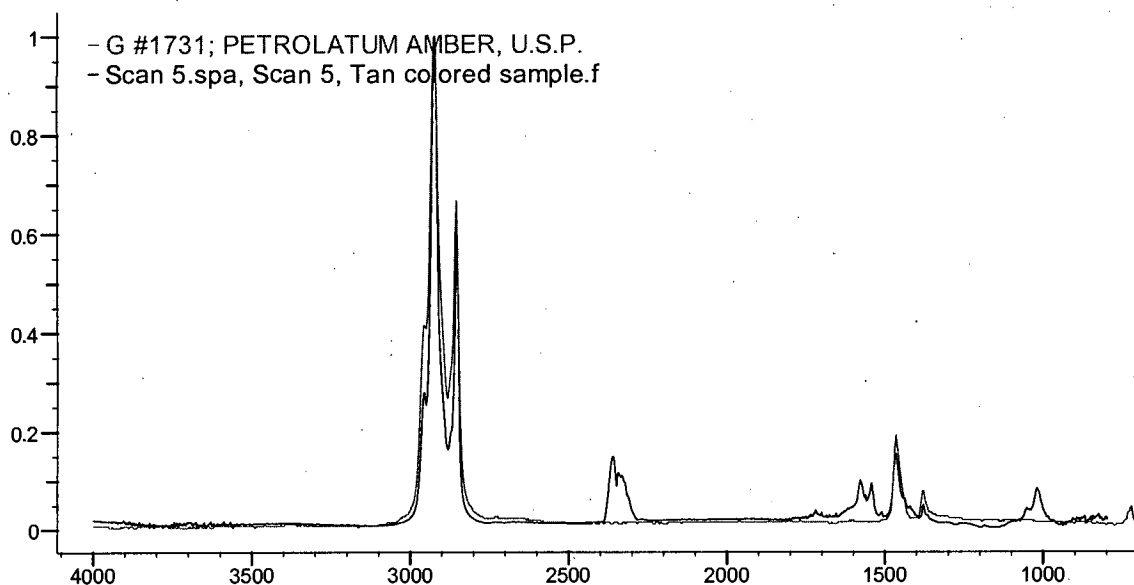


Figure 2. IR spectra of the tan-colored material (black trace) and of a hydrocarbon wax (petrolatum – red trace) from our IR library

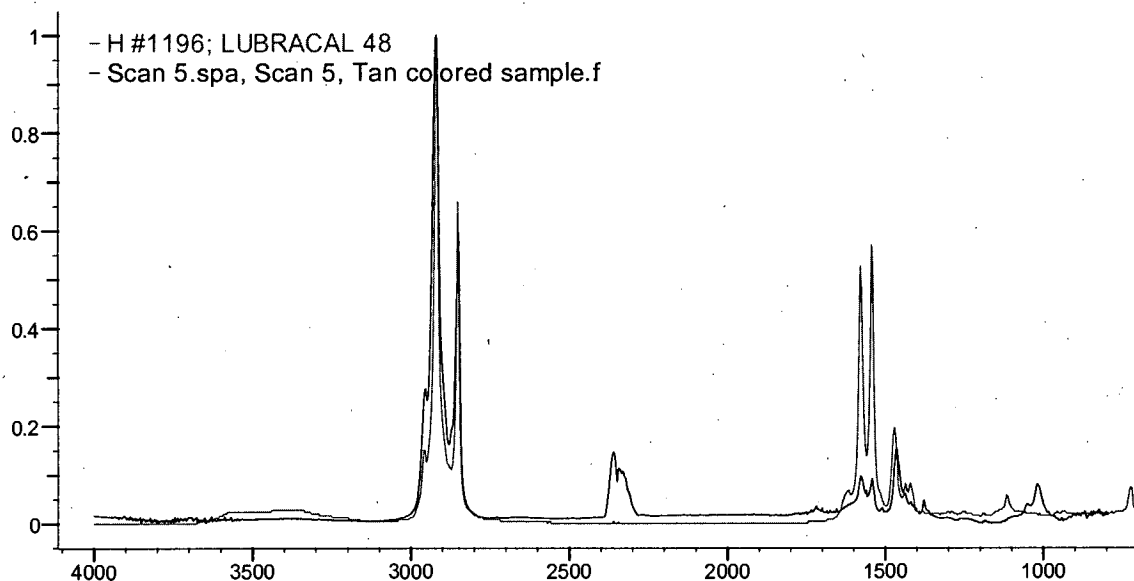


Figure 3. IR spectra of the tan-colored material (black trace) and of calcium stearate (red trace) from our IR library

Reflectance IR Survey of DCB155, DWA097, DWA158 and DWB025

date: 11/14/08

to: Doug Wall

via: DVD-via SNL (hard copy) mail

We performed a survey of coupons DCB155, DWA097, DWA158 and DWB025 using reflectance infrared (IR) spectroscopy. In these analyses an IR beam was directed to the surfaces of the coupons and reflected light collected by an arrangement of mirrors. The reflectance accessory used in these analyses is known as a "Seagull" attachment because the mirrors vaguely resemble a seagull in flight. The IR beam was directed at the surfaces of the coupons at an angle of 25° from the normal to the coupon. This angle was determined to provide the highest quality IR spectra for these coupons. The IR beam sampled an approximately 9 mm diameter circle on the surfaces of the coupons. A Fourier transform spectrometer provided the IR beam and recorded the reflectance spectra. The spectra here are plotted with the vertical axis labeled as absorbance. While, technically, for reflection spectra, the units are log (1/reflectance), the meanings of the terms are here effectively the same.

Four locations were sampled on all the coupons:

1. Location #1 is on the stamped side of the coupon, near the stamped end;
2. Location #2 is on the stamped side of the coupon, on the end opposite the stamp;
3. Location #3 is on the other side of the coupon, near the stamped end; and
4. Location #4 is on the other side of the coupon, on the end opposite the stamp.

We sampled an additional location on coupon DWB025. Location #5 is on the "other" side (opposite the stamp) of the coupon, near the mounting hole, where a deposit is especially apparent.

Figure 4 shows IR reflection spectra from locations #1 through #4 on coupon DCB155. One relatively obvious conclusion from the spectra is that the stamped side of the coupon has a much larger quantity of deposits than the other side, as indicated by the higher absorbance of their IR bands. The relatively low intensity IR bands from the other side of the coupon indicate the presence of simple hydrocarbons (bands near 2900 cm^{-1}) and silicate-based materials (bands near 1000 cm^{-1}).

The IR bands from the stamped side of coupon DCB155 have the same general frequency pattern as those obtained in transmission from material provided on a swab (Figure 5 of this report and Figure 1 of the 10/27/08 report – see above). Differences between the two spectra in the relative intensities of their IR bands are largely due to effects related to obtaining the spectra in reflection versus transmission mode. The band peaking between 2300 cm^{-1} and 2400 cm^{-1} is due to uncompensated, atmospheric CO_2 . It has no correlation to the deposits on the coupon. As noted in our 10/27/08 report, the material from the swab and, hence, the deposits on the stamped side of the coupon, are a mixture of hydrocarbons, carboxylic acid salts and silicate-based materials.

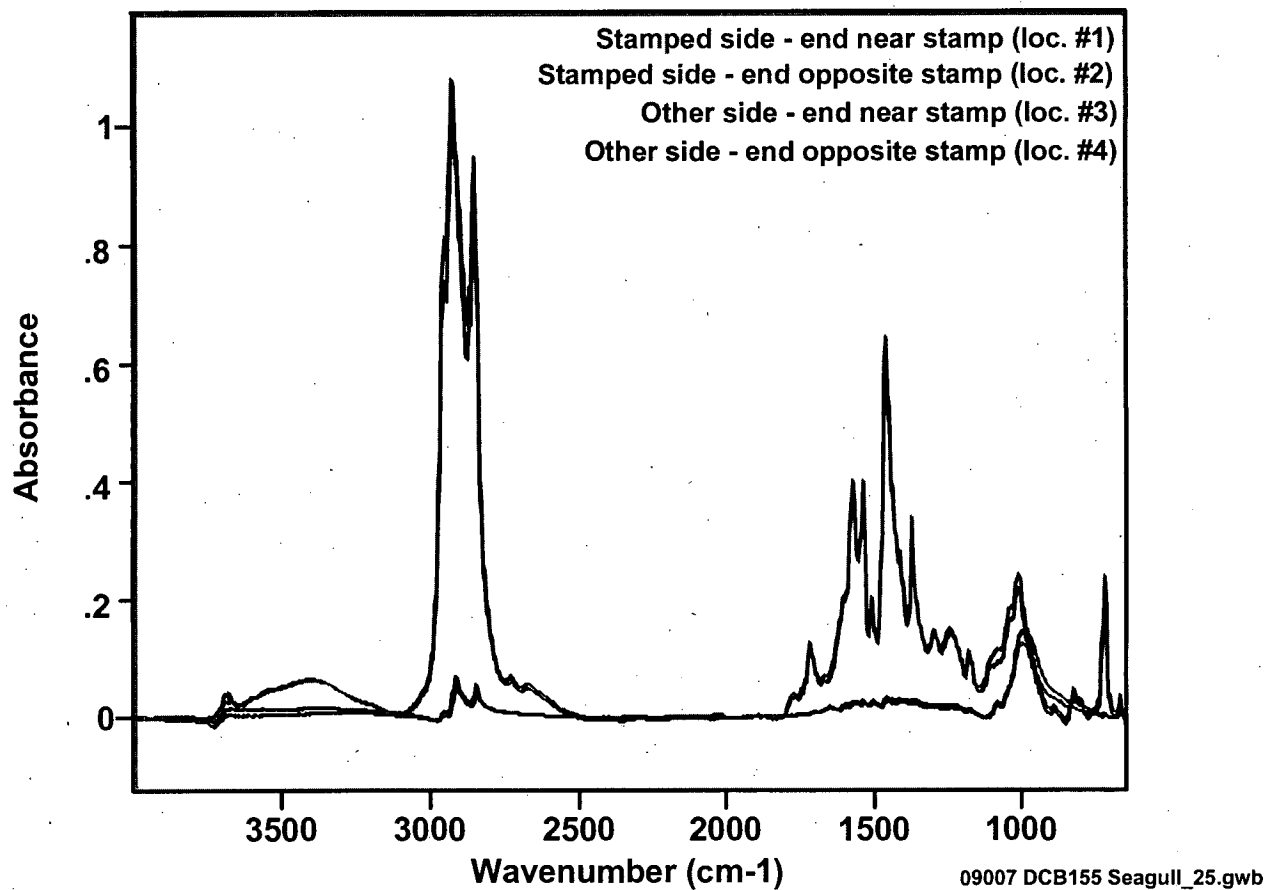


Figure 4. Reflection IR spectra of DCB155

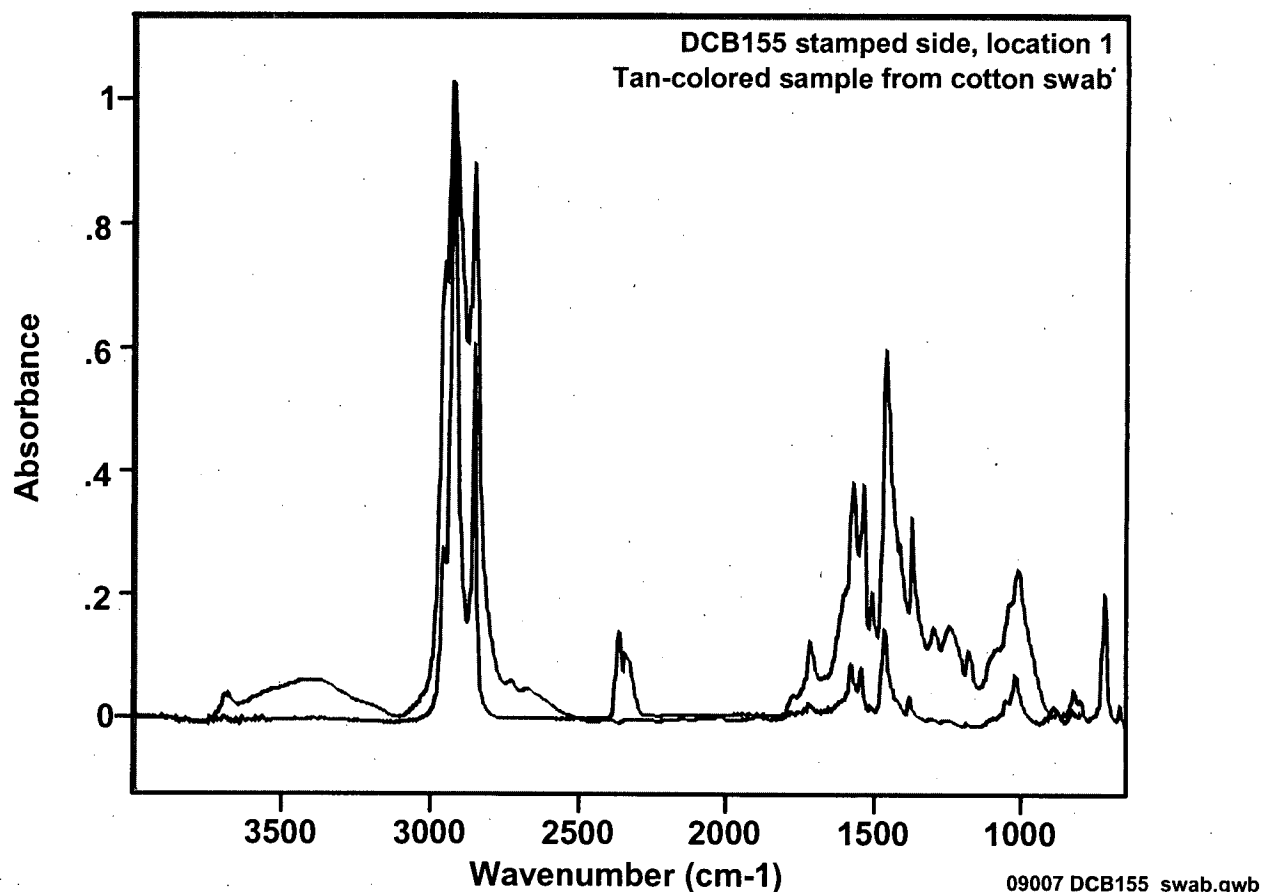


Figure 5. IR reflection spectrum of DCB155 and IR transmission spectrum of swab sample

Figure 6 shows IR reflection spectra from locations #1 through #4 on coupon DWA097. The intensities of the spectra from coupon DWA097 are roughly at the level of those from the other side of coupon DCB155 (the less contaminated side). For coupon DWA097 the most intense spectra come from locations #2 and #4 – the end opposite the stamp on both sides of the coupon. From comparison to spectra in our IR library, we find several possibilities for the material in locations #2 and #4, including an epoxy resin and a cellulose-filled resin. The lower intensity IR spectra from locations #1 and #3 (both sides, end near stamp) are due to hydrocarbons and silicate-based materials.

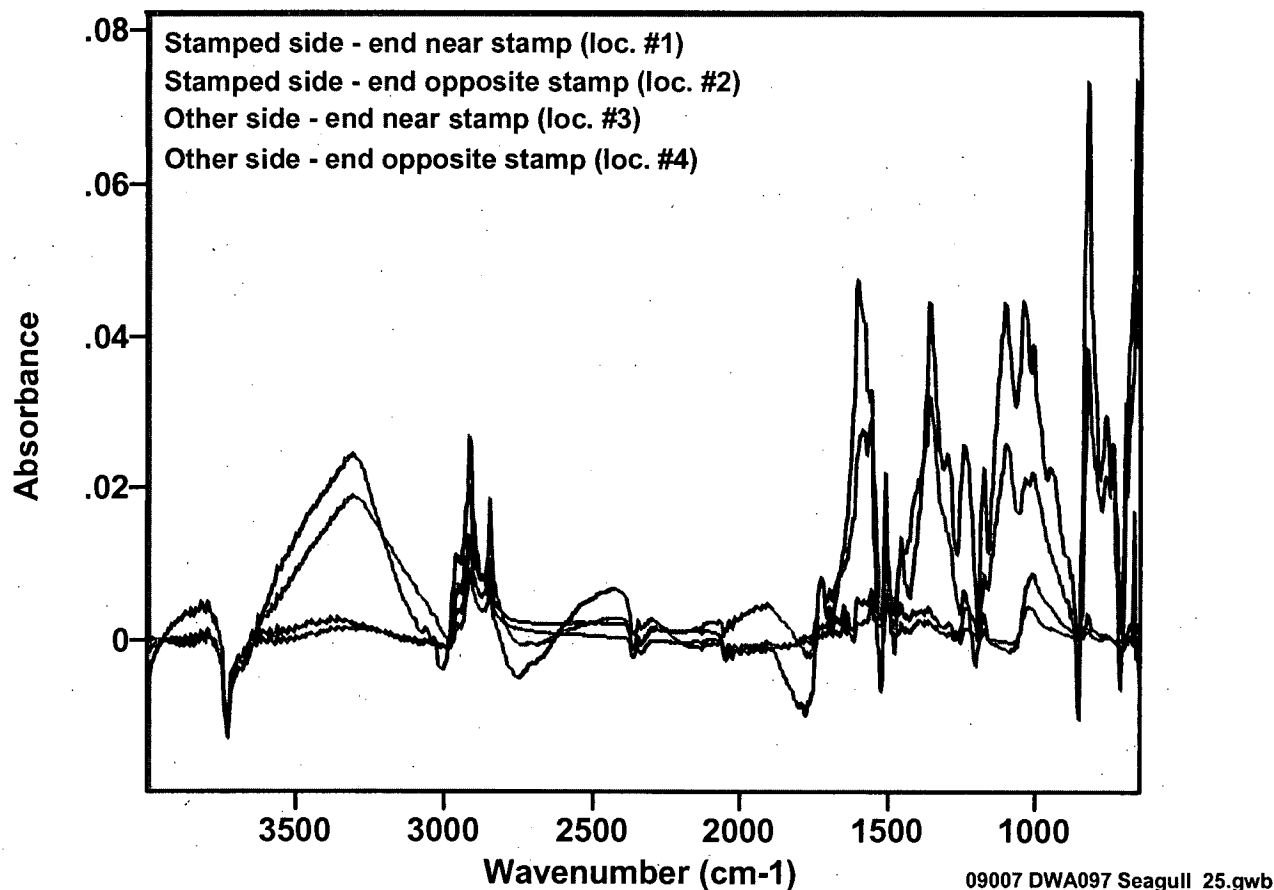


Figure 6. Reflection IR spectra of DWA097

Figure 7 shows IR reflection spectra from locations #1 through #4 on coupon DWA158. The intensities of the spectra from coupon DWA158 are also roughly at the level of those from the other side of coupon DCB155 (the less contaminated side). The locations on the stamped side (#1 and #2) of coupon DWA158 yielded more intense spectra than the other side. The spectra are, however, similar in pattern and indicate the presence of, primarily, simple hydrocarbons and silicate-based materials.

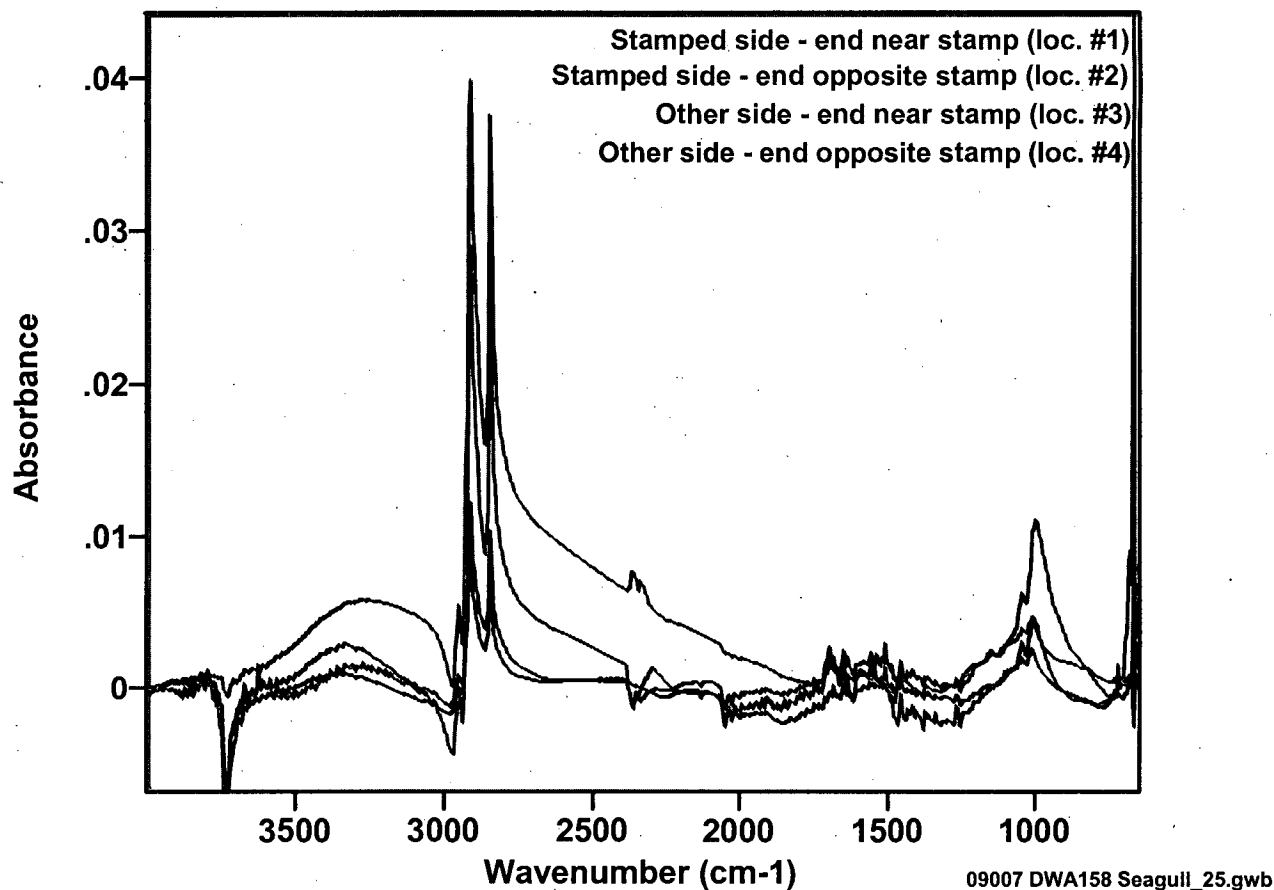


Figure 7. Reflection IR spectra of DWA158

Figure 8 shows IR reflection spectra from locations #1 through #5 on coupon DWB025. The intensities of the spectra from locations #1 through #4 on coupon DWB025 are, again, roughly at the level of those from the other side of coupon DCB155 (the less contaminated side). Simple hydrocarbons are present in the spectra from locations #1 through #4. The spectrum from location #5 (other side, near the mounting hole) of coupon DWB025 is significantly more intense than those from the other locations. The spectrum from location #5 indicates that nitrate salts and cellulose-based materials, possibly also with silicate-based materials and hydrogen carbonates, make up the deposit at this location. Smaller amounts of these materials are present in locations #1 and #3.

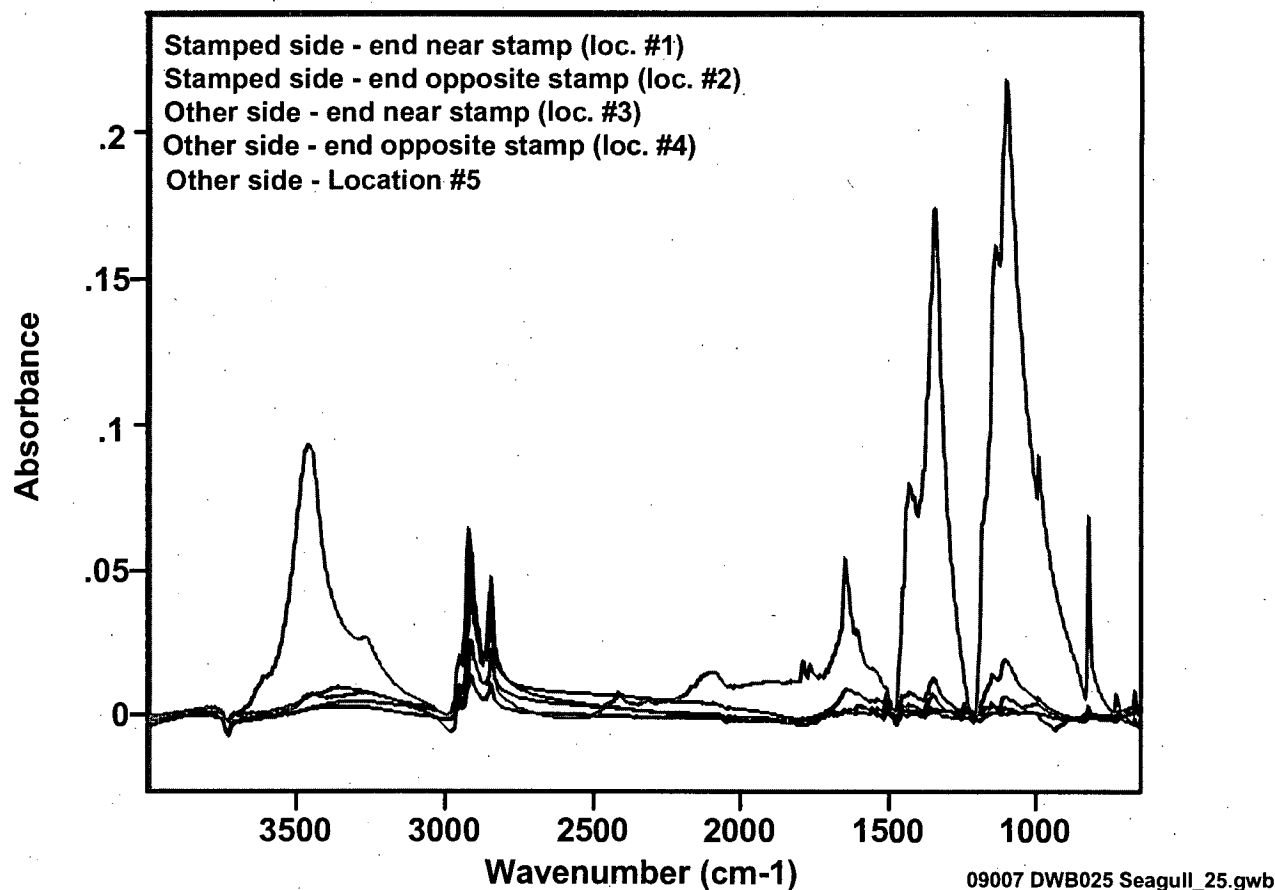


Figure 8. Reflection IR spectra of DWB025

A mixture of hydrocarbons, carboxylic acid salts and silicate-based materials make up the deposit on the stamped side of coupon DCB155, which is much more concentrated than the deposits on the other side of coupon DCB155. The deposits on the other coupons are at the relatively low concentration level of those on the other side of coupon DCB155, except for those at location #5 on coupon DWB025. There is, however, significant side-to-side and end-to-end variation of the concentrations of the deposits on all the coupons.

Reflectance IR Survey of DCB089, DWA099, DCA120 and DWA138

date: 12/3/08

to: Doug Wall

via: DVD-via SNL (hard copy) mail

IR spectra were obtained in reflection as described in the first paragraph of the previous (11/14/08) report. A single beam spectrum of coupon DCB200 was used as the background spectrum. Three locations were sampled on all the coupons:

1. Location #1 is on the stamped side of the coupon, near the stamped end;
2. Location #2 is on the stamped side of the coupon, on the end opposite the stamp; and
3. Location #3 is on the other side of the coupon, near the stamped end.

The IR spectra from DCB089, DWA099, DCA120 and DWA138 are plotted in Figures 9-12. All of the spectra show bands due to alkane hydrocarbons, specifically C-H stretching modes between 2800 cm^{-1} and 3000 cm^{-1} . Absorptivities of these bands were determined and published by S. A. Francis (Anal. Chem. **25**[10], [1953], 1466). From these absorptivities and treating the IR reflection absorbances as equivalent to double pass transmission measurements (the IR beam is assumed to pass through the deposit, reflect off the metal substrate and complete a second pass through the deposit), we can make a rough estimate the amount of hydrocarbons in the deposit. Calculating in this manner, a C-H stretching mode absorbance of 0.1 corresponds roughly to $10\text{ }\mu\text{g/cm}^2$ of hydrocarbon. The amount of hydrocarbon will scale proportionately with the absorbance.

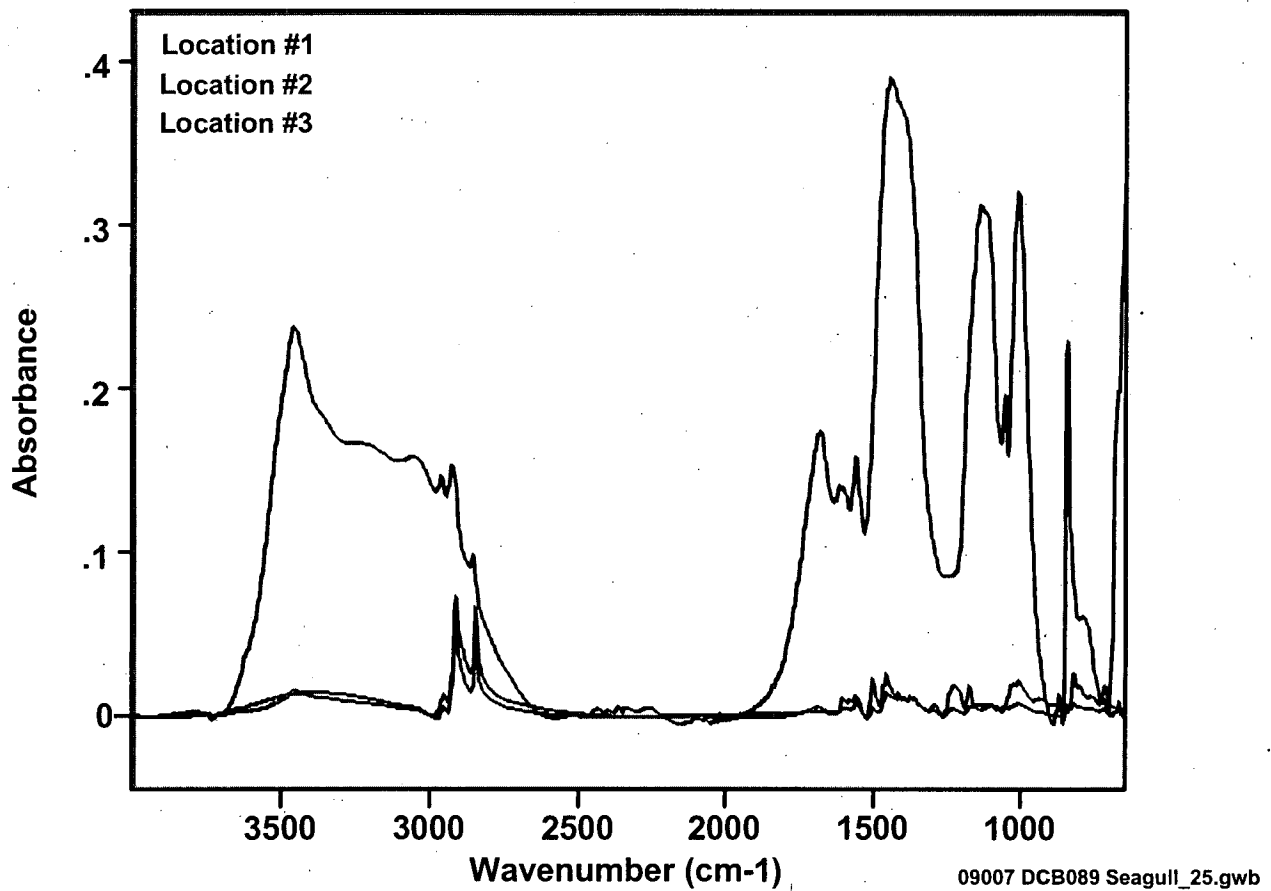


Figure 9. Reflection IR spectra of DCB089

The spectra from all three locations of DCB089 (Figure 9) show alkane C-H bands (again, 2800 cm^{-1} to 3000 cm^{-1}) at absorbances of 0.05 to 0.1 units. The species represented by the C-H bands may be simple, long-chain hydrocarbons, such as oils, greases, etc. The spectrum from location #2 includes other, lower intensity bands that may be due to an epoxy resin. The spectrum from location #3 includes much more intense bands due to much thicker deposits of inorganic materials. These thicker deposits are most likely a mixture of carbonates and silicates.

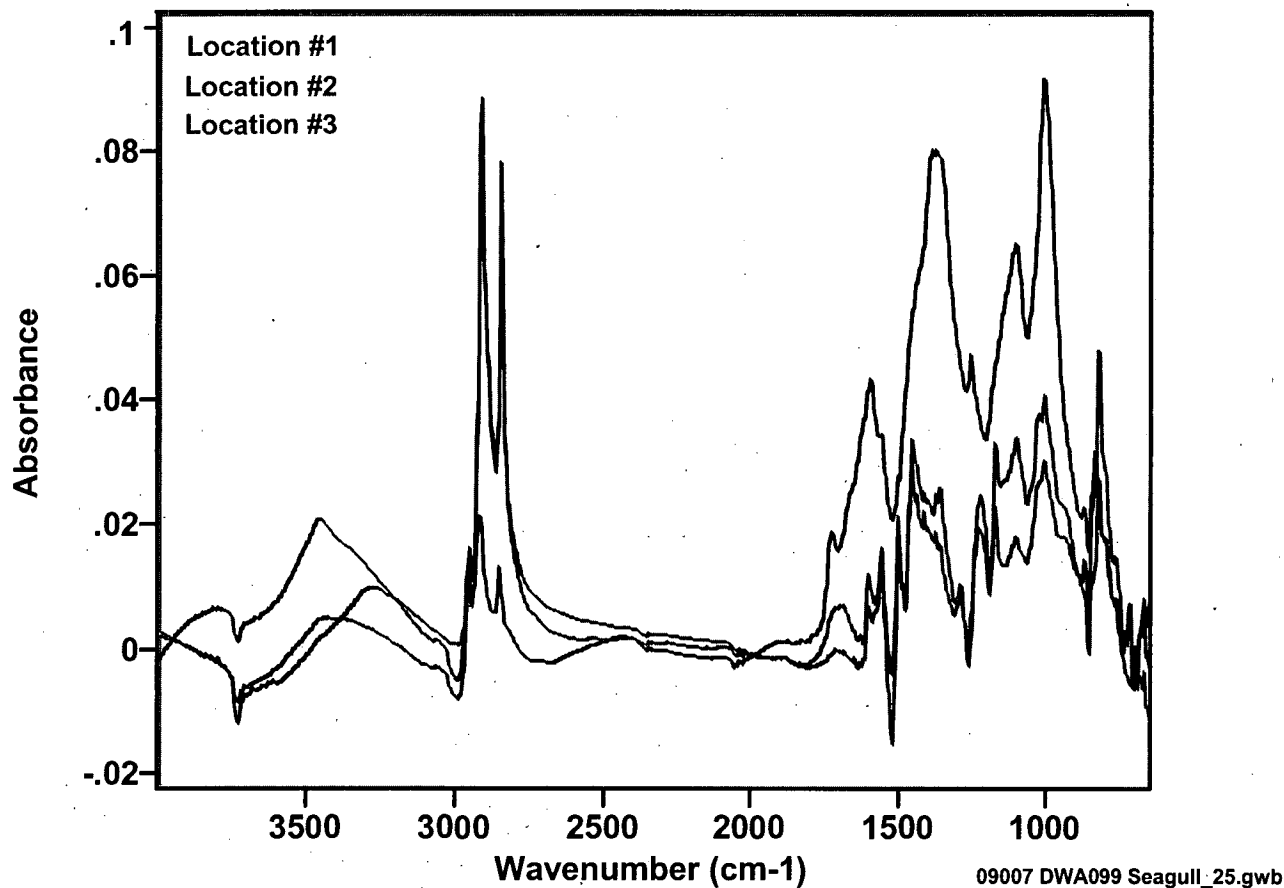


Figure 10. Reflection IR spectra of DWA099

Hydrocarbon bands from locations #1 and #2 of sample DWA099 (Figure 10) have an intensity of about 0.1 absorbance unit. The hydrocarbons at these locations are believed to be primarily long-chain, alkane hydrocarbons, but lower intensity and lower frequency (1800 cm^{-1} to 700 cm^{-1}) bands in these spectra suggest the presence of phenolic resins. The spectrum from location #3 has lower intensity hydrocarbon bands (about 0.02 absorbance units), and the spectrum is dominated by lower frequency bands related to deposits of nitrate salts and silicates.

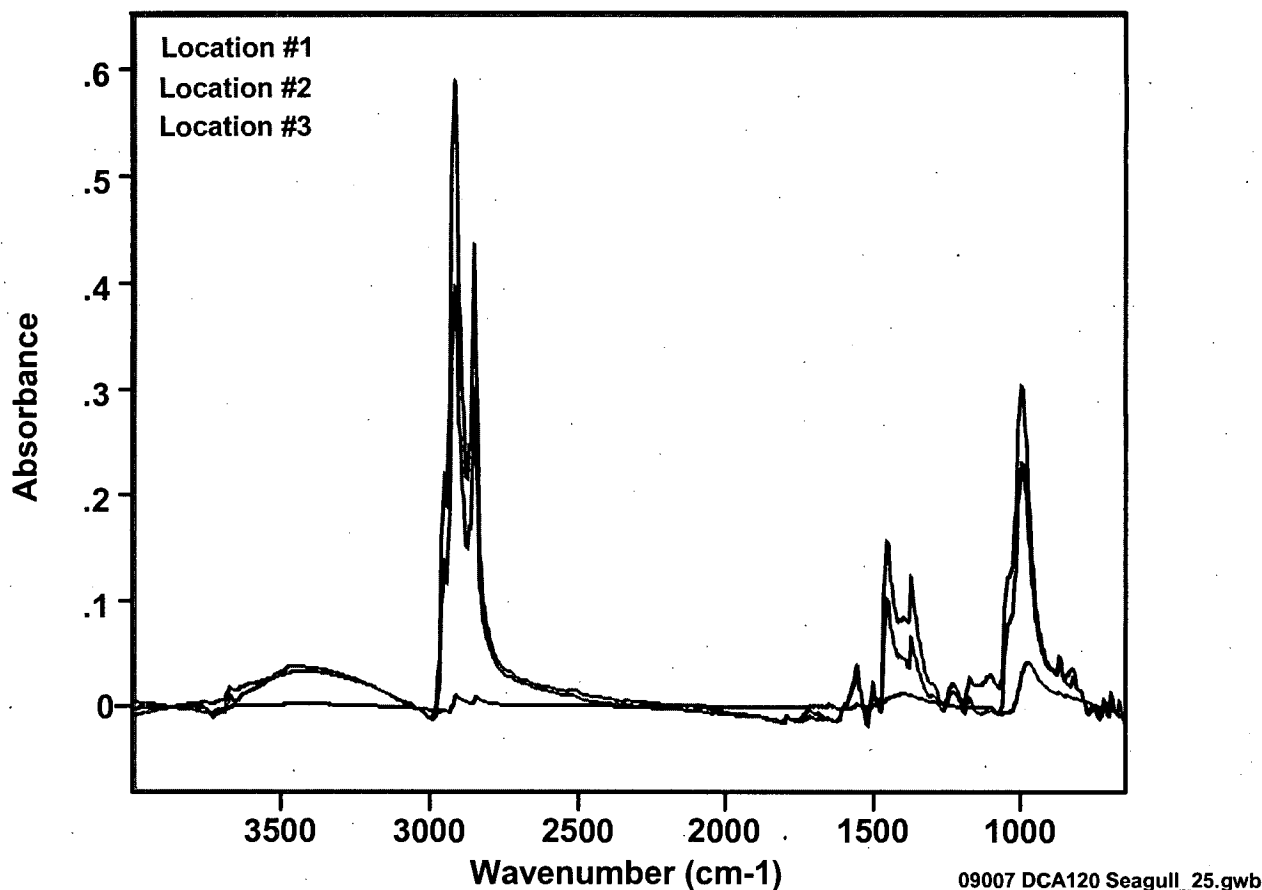
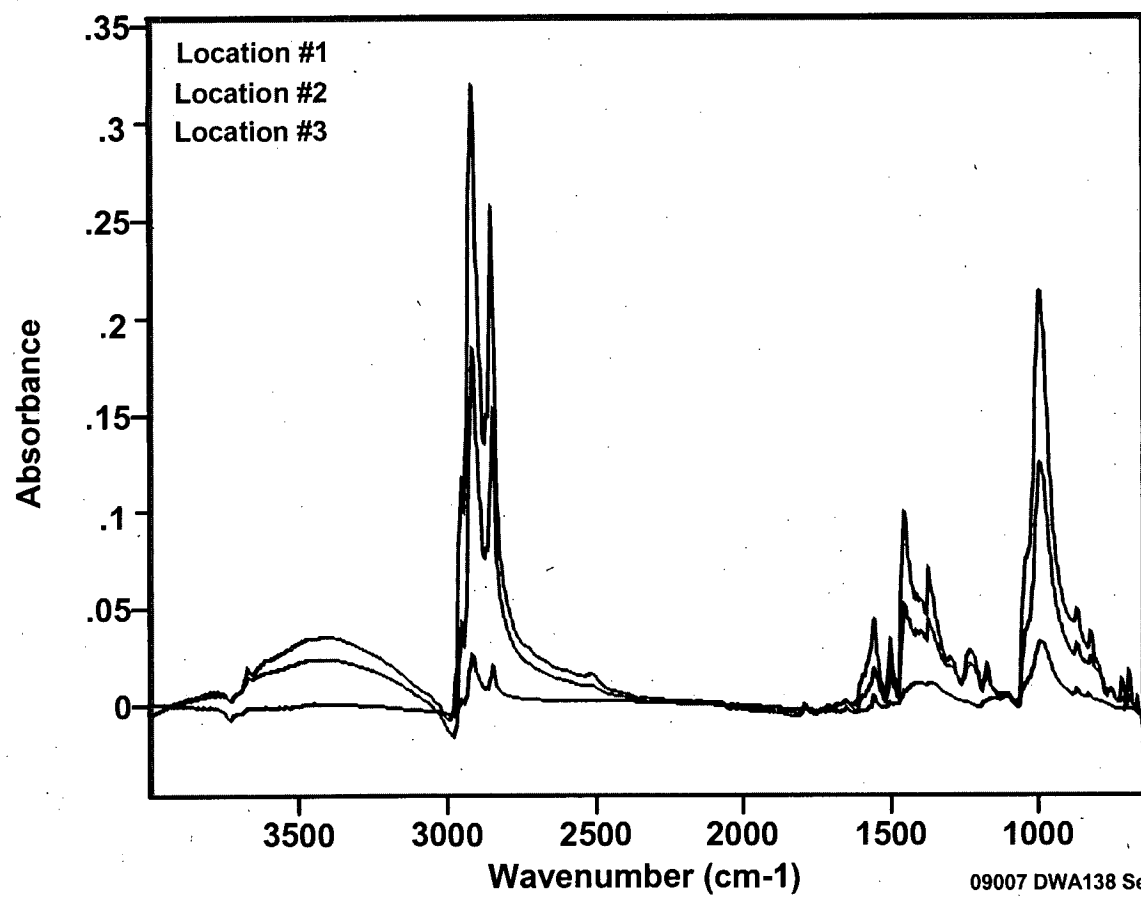


Figure 11. Reflection IR spectra of DCA120

The IR spectra from samples DCA120 (Figure 11) and DWA138 (Figure 12) are, except for intensity, nearly identical in band patterns. Spectra from locations #2 of DCA120 and DWA138 are plotted for comparison in Figure 13. In terms of intensity, the IR bands from DCA120 are about twice those from DWA138, with a maximum absorbance of about 0.6 units in the spectra from DCA120 and a maximum absorbance of about 0.3 units in the spectra from DWA138. The overall pattern of intensities between the locations in the samples is also similar, with location #2 yielding the most intense bands, location #1 yielding bands of lower intensity and location #3 yielding much less intense bands, with a somewhat different pattern compared to locations #1 and #2.

The simplest identification of the materials represented by the IR spectra from samples DCA120 and DWA138 is that they are comprised of a long-chain, alkane hydrocarbon (grease, oil or polyethylene-like polymer) plus a silicate (bands peaking near 1000 cm⁻¹). However, an alternate identification is that the material is an organophosphite/phosphate ester, such as are used as stabilizers, corrosion inhibitors and lubricant additives.



09007 DWA138 Seagull_25.gwb

Figure 12. Reflection IR spectra of DWA138

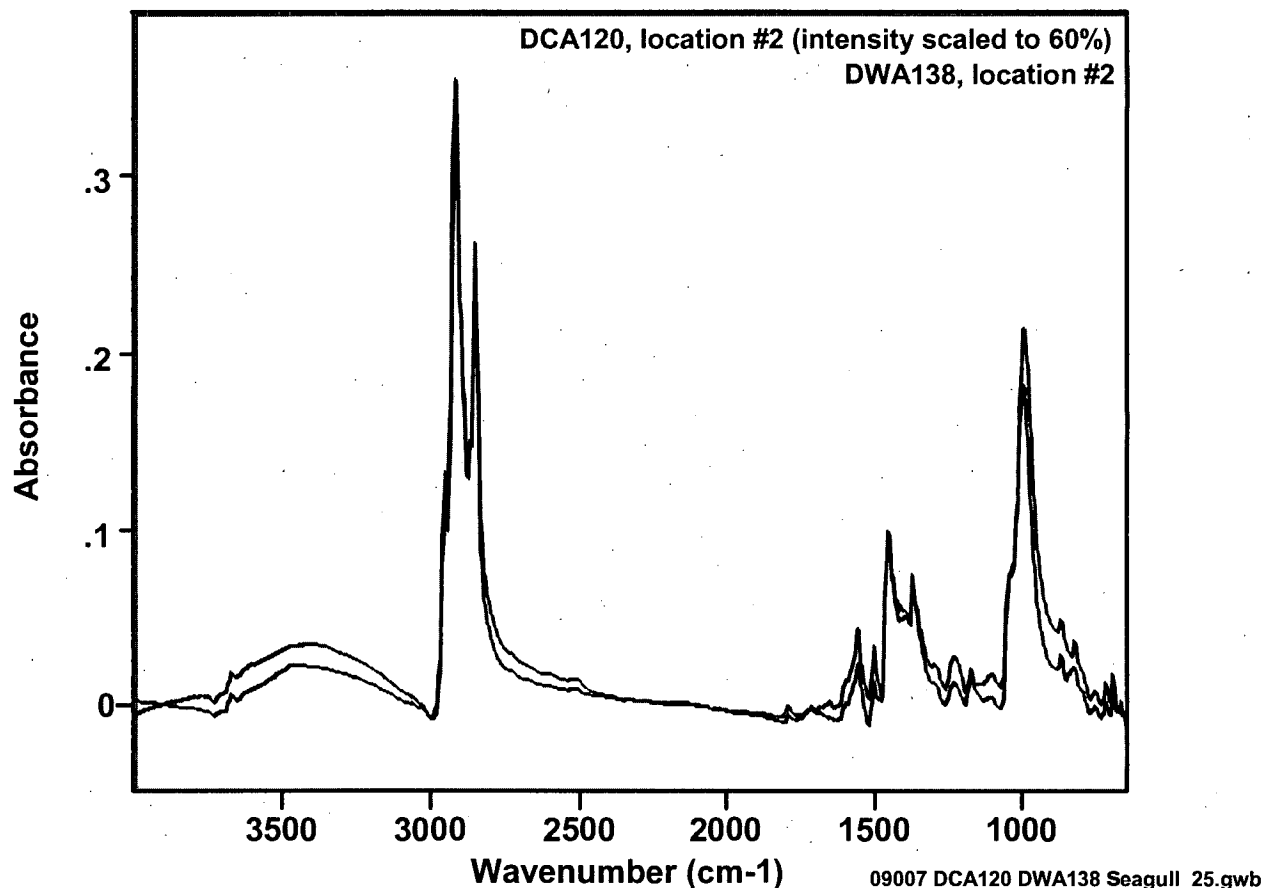


Figure 13. Comparison of reflection IR spectra from samples DCA120 and DWA138

Reflectance IR Survey of DCA288 (reference), ACA156 and BCC155

date: 1/16/09

to: Ed Lopez, Doug Wall

via: voice mail, DVD via SNL mail (respectively)

We obtained IR reflection spectra of reference coupon DCA288 and coupons ACA156 and BCC155 as described in the first paragraph of the 11/14/08 Preliminary Report (above) and at the locations described in the second paragraph of the 11/14/08 report. The spectrum of coupon DCA288 was referenced (ratioed) to the spectrum of a gold mirror (essentially featureless in the IR), and the spectra of ACA156 and BCC155 were referenced to the spectrum of the reference coupon, DCA288. The IR spectrum of DCA288 and the spectra (four locations each) from ACA156 and BCC155 are shown, respectively, in Figures 14, 15 and 16.

The spectrum of reference coupon DCA288 (Figure 14) indicates that its surface has, compared to our gold mirror reference, less hydroxyl (probably absorbed water) and alkane

contamination but more silicate deposits. Note the negative-pointing "O-H" and "Alkane C-H" bands and the positive-pointing "Si-O" bands in the spectrum. The gold mirror was cleaned prior to the recording of its spectrum, but it was not put through an extremely rigorous cleaning procedure. Also, the overall intensities of the bands are low, so that the differences in the amounts of material are small. Nevertheless, the spectra indicate that the surface of coupon DCA288 is relatively clean.

The spectra of coupons ACA156 and BCC155 (Figures 15 and 16) indicate that their surfaces have slightly more hydroxyl (probably absorbed water), alkane hydrocarbons and metal oxides (probably chromium and molybdenum oxides) than reference coupon DCA288. Their IR spectra show no distinct evidence of other contaminants. Again, however, the overall band intensities are small, so that the amounts of contaminant materials are small. Specifically, the intensities of the "Alkane C-H" (hydrocarbon) bands are of the order of a milli-absorbance unit, which roughly corresponds to $0.2 \mu\text{g}/\text{cm}^2$ of hydrocarbon, or a layer a few nanometers thick.

We understand that coupons ACA156 and BCC155 were rigorously cleaned to remove (hydrocarbon) contamination. The cleaning appears to have been largely successful. The remaining hydrocarbons on these coupons are present at the few monolayer level, much less than the contamination identified on coupons previously analyzed (see the previous preliminary reports).

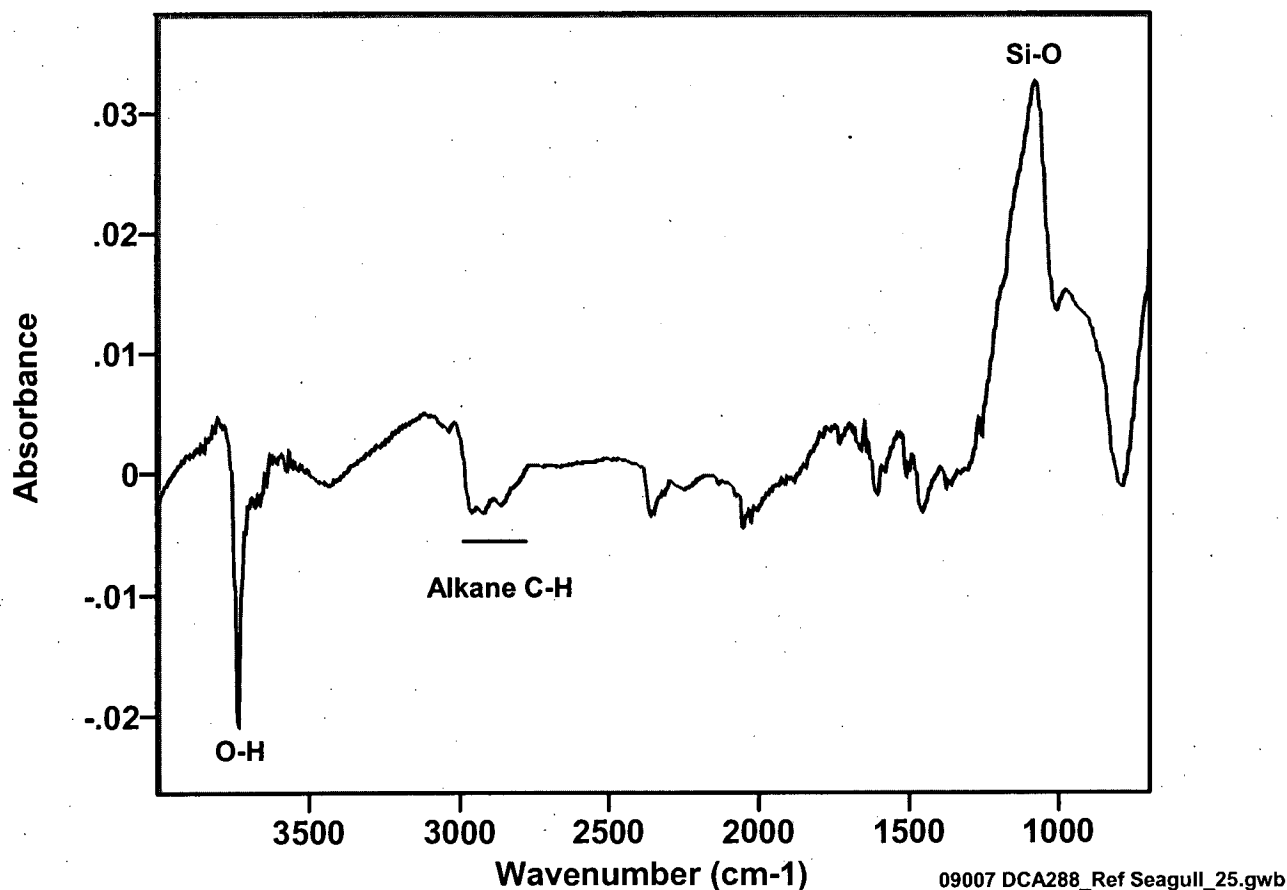


Figure 14. Reflectance IR spectrum of Reference Coupon DCA288 (vs gold mirror)

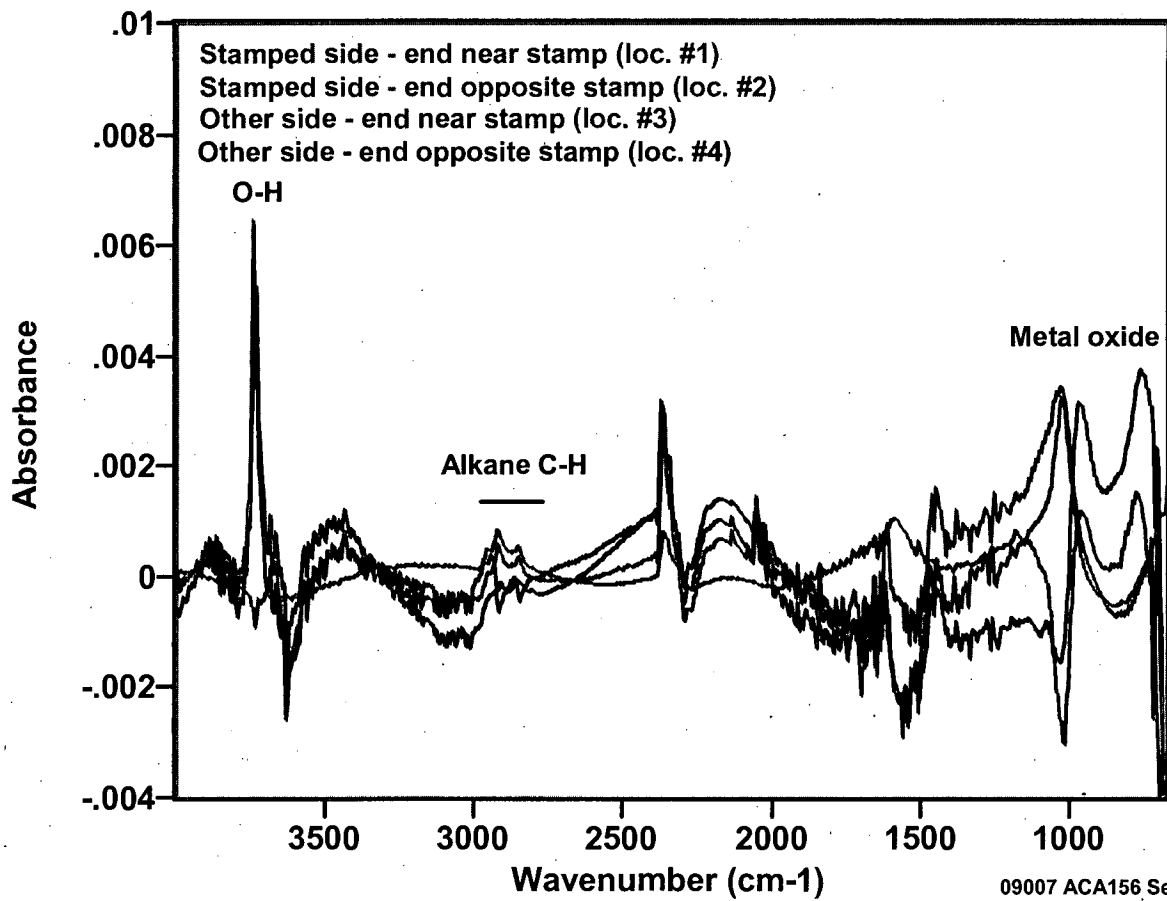


Figure 15. Reflectance IR spectrum of coupon ACA156 (vs DCA288)

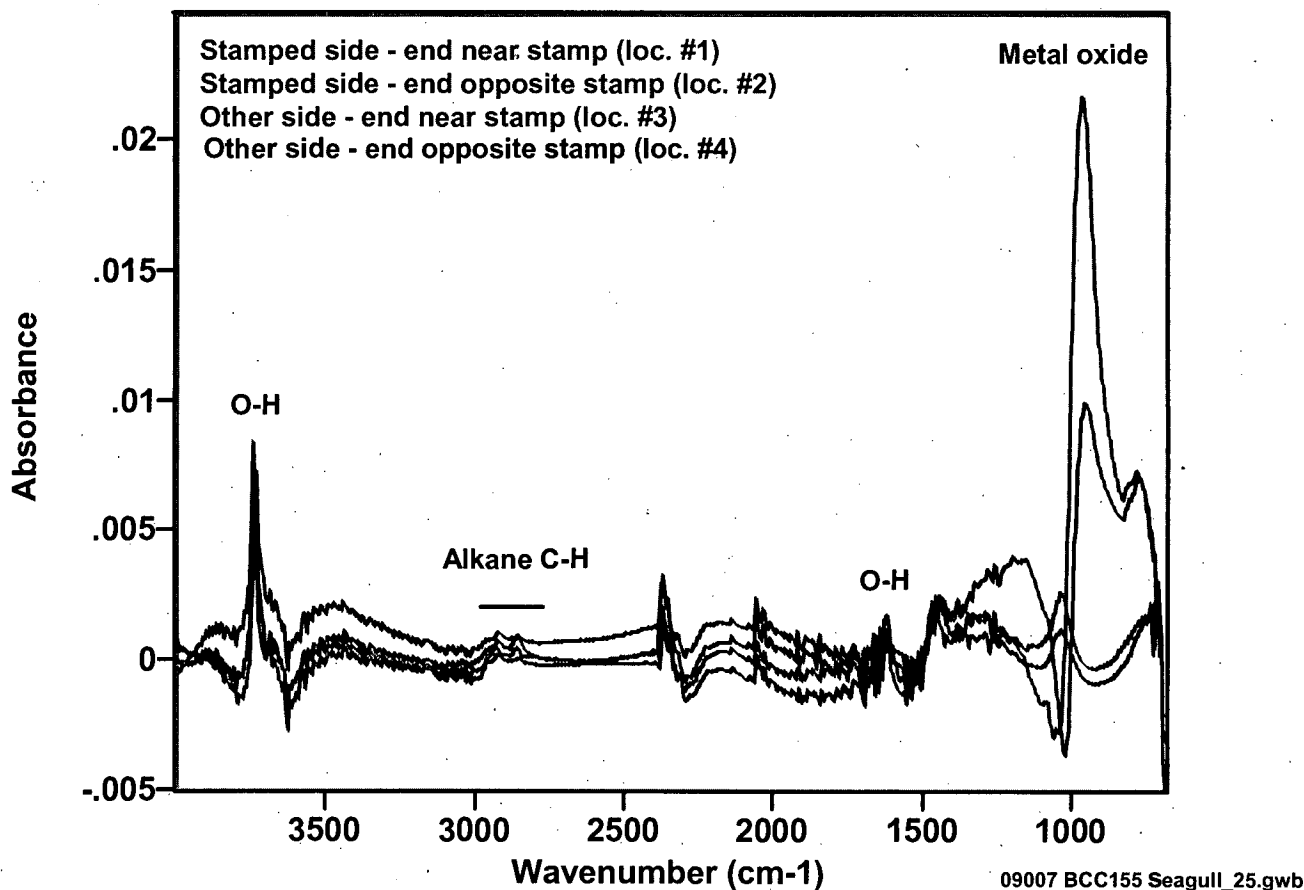


Figure 16. Reflectance IR spectrum of coupon BCC155 (vs DCA288)

Reflectance IR Survey of DWA098, DWA100, DWB098, DWB099 and DWB100

date: 3/13/09

to: Doug Wall

via: DVD-via SNL (hard copy) mail

We obtained IR reflection spectra of reference coupon DCB200 and coupons DWA098, DWA100, DWB098, DWB099 and DWB100 as described in the first paragraph of the 11/14/08 Preliminary Report (above) and at the locations described in the second paragraph of the 11/14/08 report. Single beam spectra of coupons DWA098, DWA100, DWB098, DWB099 and DWB100 were ratioed to that of the DCB200 reference coupon to compensate for the spectral responses of the Fourier transform spectrometer and the Alloy 22 substrate.

Infrared (IR) spectra from the five coupons are shown in Figures 17-21. A contaminant not previously identified is typified by the spectrum from location #4 on coupon DWA098 (Figure 17). This spectrum is similar to that of a butyl rubber/resin-based material, apparently mixed with a silicate filler. The silicate filler is most likely Montmorillonite clay. One application for the material composing this contaminant is as an adhesive or flow additive in an asphalt sealant or cement (such as roofing cement). In this report we will refer to this contaminant as "rubber/resin". Location #4 on coupon DWA100 yields an IR spectrum (Figure 18) that indicates the presence of relatively thick (note absorbance intensities near 0.8) deposits of hydrated nitrates. Raman spectra are consistent with this identification. Location #4 on coupon DWB098 yields an IR spectrum (Figure 19) very similar to the IR spectrum from location #3 on coupon DCB089 (see Figure 9, above). We previously identified this spectral pattern as characteristic of carbonate and silicate deposits. We label as "hydrocarbons" materials associated with IR bands characteristic of long-chain alkane species (could be oils, greases, fatty acids or their salts) but not more specifically identifiable.

Table 1, below, summarizes the information in the IR spectra obtained at four locations on each coupon. This table lists the primary contaminant (the one with the most intense IR bands) and other contaminants which we identified from their IR bands. The third column lists the intensities of a band due to methylene ($-\text{CH}_2-$) C-H stretching vibrations, which is due to alkane hydrocarbon chains and peaks near 2920 cm^{-1} . Alkane hydrocarbon chains are found in the organic constituents (oils, rubber/resin, fatty acids, etc.) identified in the contaminant deposits. The intensity of this band is a measure of the amount of "equivalent" hydrocarbon in the contaminant deposit. Assuming that the IR reflection measurements are equivalent to a double-pass transmission measurement (the IR beam passes through the contaminant, reflects off the metal substrate surface and then makes a second pass through the contaminant before it encounters the collection optics), 1 milliabsorbance (mAbs, or 0.001 absorbance) unit at the peak of the 2920 cm^{-1} band corresponds approximately to $0.1\text{ }\mu\text{g/cm}^2$ density, or 1 – 2 nm thickness, of equivalent hydrocarbon.

Table 1. Compositions of Deposits on Coupons DWA098, DWA100, DWB098, DWB099 and DWB100

Coupon	Location*	C-H intensity** mAbs units	Major Contaminant	Other Contaminants
DWA098	1	47	Hydrocarbons & rubber/resin	Carbonate and silicate inorganics
	2	82	Hydrocarbons & rubber/resin	Carbonate and silicate inorganics
	3	9	Carbonate and silicate inorganics	Rubber/resin
	4	29	Rubber/resin (Butyl rubber- and resin-based material, with a silicate (likely Montmorillonite clay) filler	Carbonate and silicate inorganics
DWA100	1	43	Hydrocarbons & rubber/resin	Carbonate and silicate inorganics
	2	22	Carbonate and silicate inorganics	Hydrocarbons
	3	18	Hydrated nitrates	Hydrocarbons
	4	40	Hydrated nitrates	Hydrocarbons
DWB098	1	54	Hydrocarbons	Miscellaneous inorganics
	2	368	Rubber/resin	Carbonate and silicate inorganics
	3	5	Carbonate and silicate inorganics	Hydrocarbons
	4	59	Carbonate and silicate inorganics	Hydrocarbons
DWB099	1	76	Epoxy/phenolic & hydrocarbons	Miscellaneous inorganics
	2	318	Rubber/resin	Carbonate and silicate inorganics
	3	6	Carbonate and silicate inorganics	Hydrocarbons
	4	32	Carbonate and silicate inorganics	Hydrocarbons
DWB100	1	105	Epoxy/phenolic & hydrocarbons	Miscellaneous inorganics
	2	103	Epoxy/phenolic & hydrocarbons	Miscellaneous inorganics
	3	8	Carbonate and silicate inorganics	Hydrocarbons
	4	26	Rubber/resin	Carbonate and silicate inorganics

* Location #1 is on the stamped side of the coupon, near the stamped end;
 Location #2 is on the stamped side of the coupon, on the end opposite the stamp;

Location #3 is on the other side of the coupon, near the stamped end; and
Location #4 is on the other side of the coupon, on the end opposite the stamp.

** Peak absorption intensity (milli-absorbance units) of the methylene ($-\text{CH}_2-$) C-H stretch mode, peaking near 2920 cm^{-1} ; obtained using the GRAMS/Integrate application with a custom baseline for each spectrum

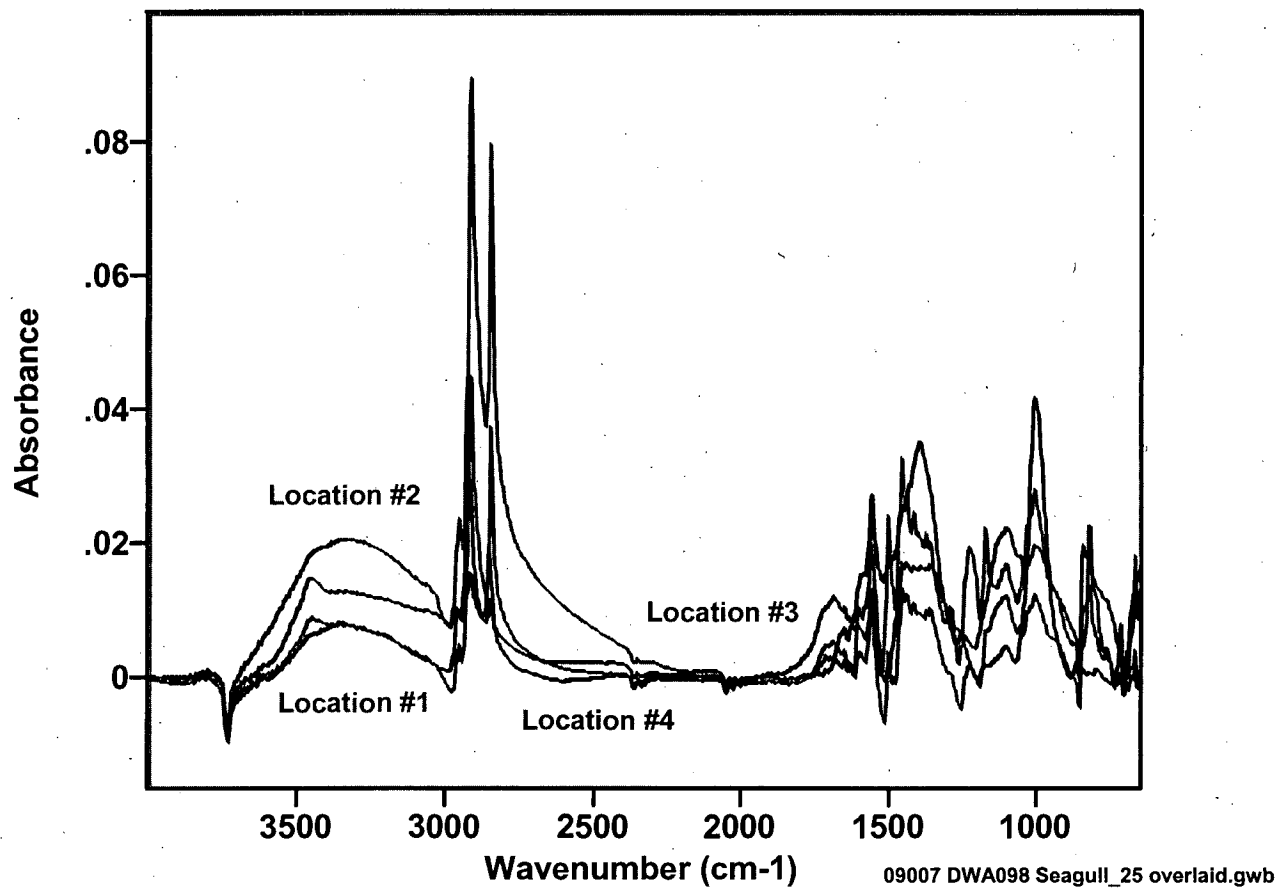


Figure 17. Reflection IR spectra of Coupon DWA098 (60C) vs DCB200 (reference)

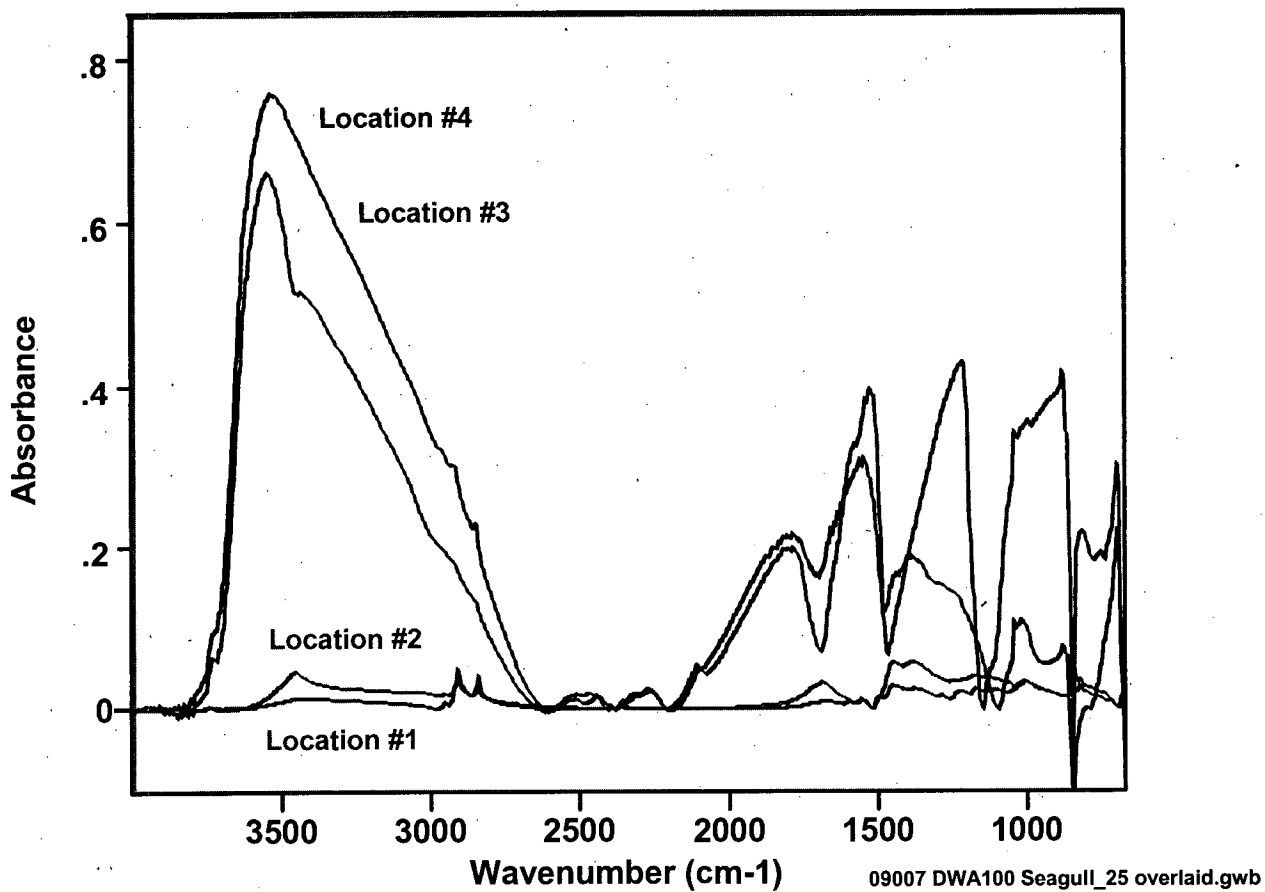
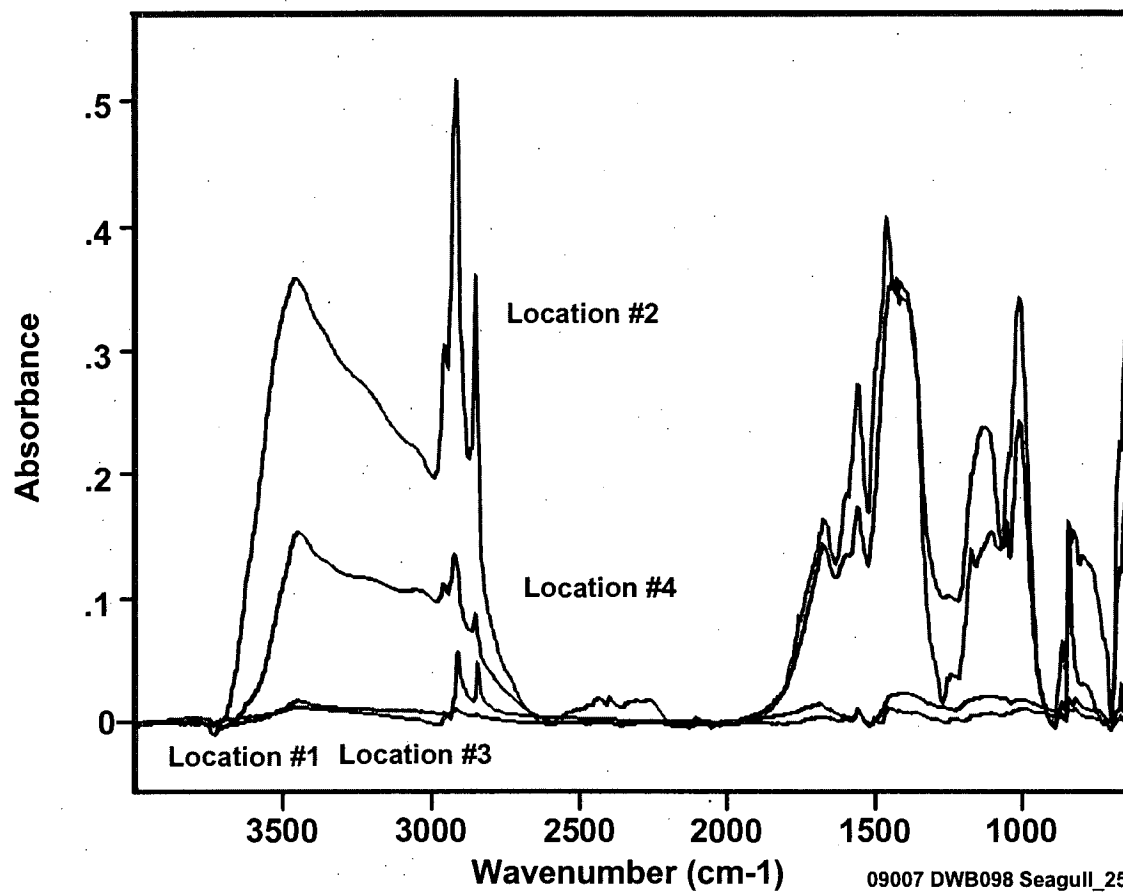


Figure 18. Reflection IR spectra of Coupon DWA100 (60C) vs DCB200 (reference)



09007 DWB098 Seagull_25 overlaid.gwb

Figure 19. Reflection IR spectra of Coupon DWB098 (60C) vs DCB200 (reference)

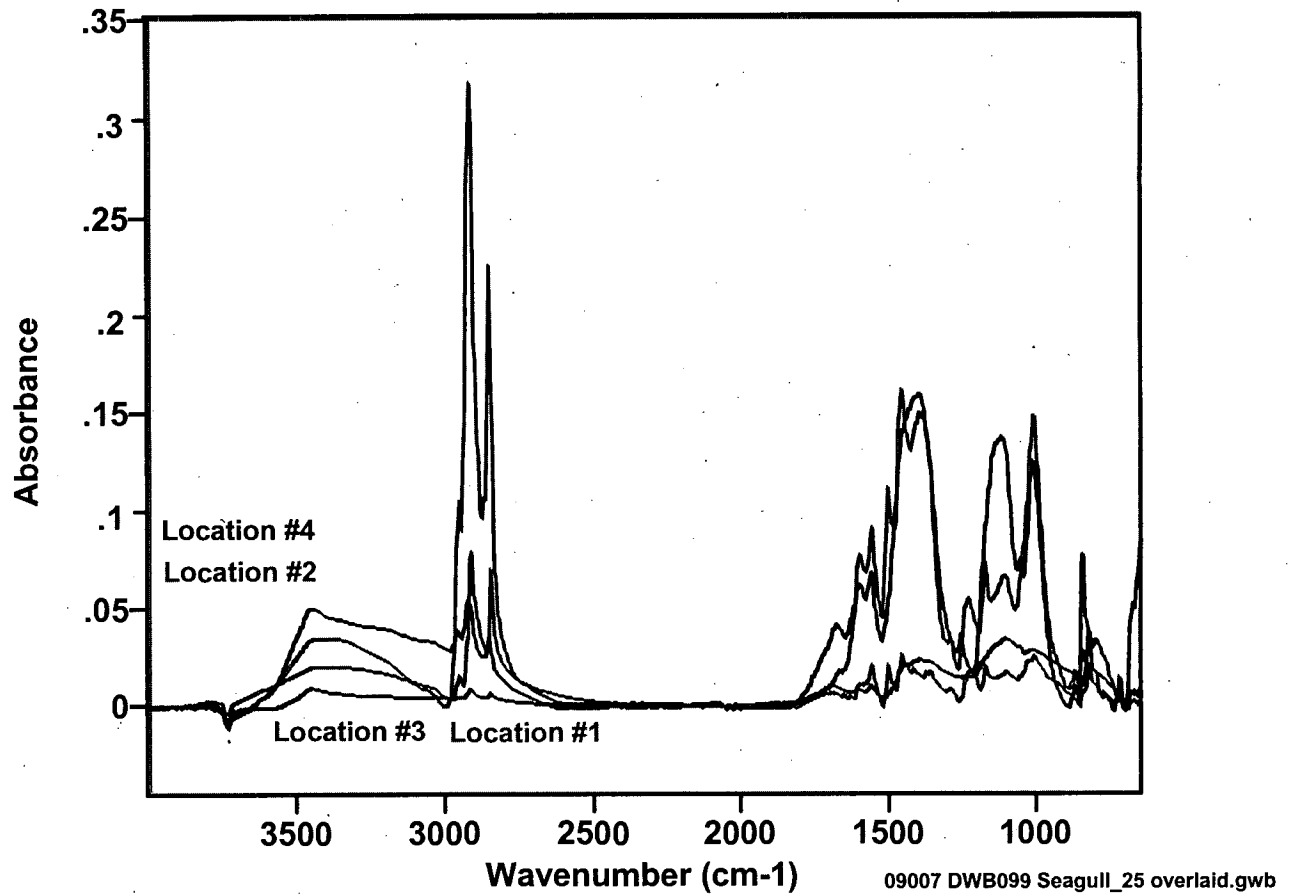


Figure 20. Reflection IR spectra of Coupon DWB099 (60C) vs DCB200 (reference)

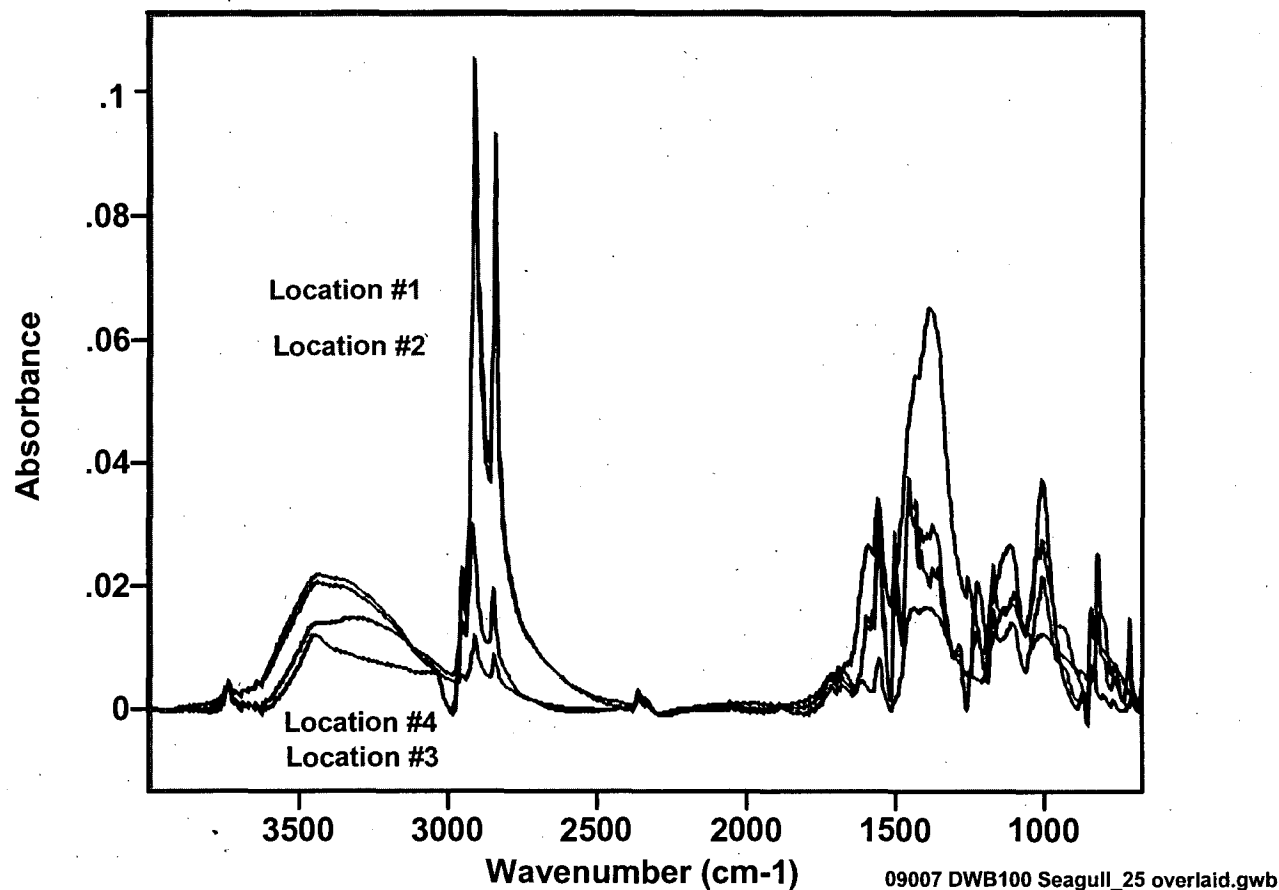


Figure 21. Reflection IR spectra of Coupon DWB100 (60C) vs DCB200 (reference)

Final Report

date:

Analysts:

Bertha M. Montoya

Org. 1822

Ph: 844-2489

Fax: 844-9781

E-mail: bmmonto@sandia.gov

Staff Contact:

D. R. Tallant

Org. 1822

Ph: 844-3629

Fax: 844-9781

E-mail: drtalla@sandia.gov