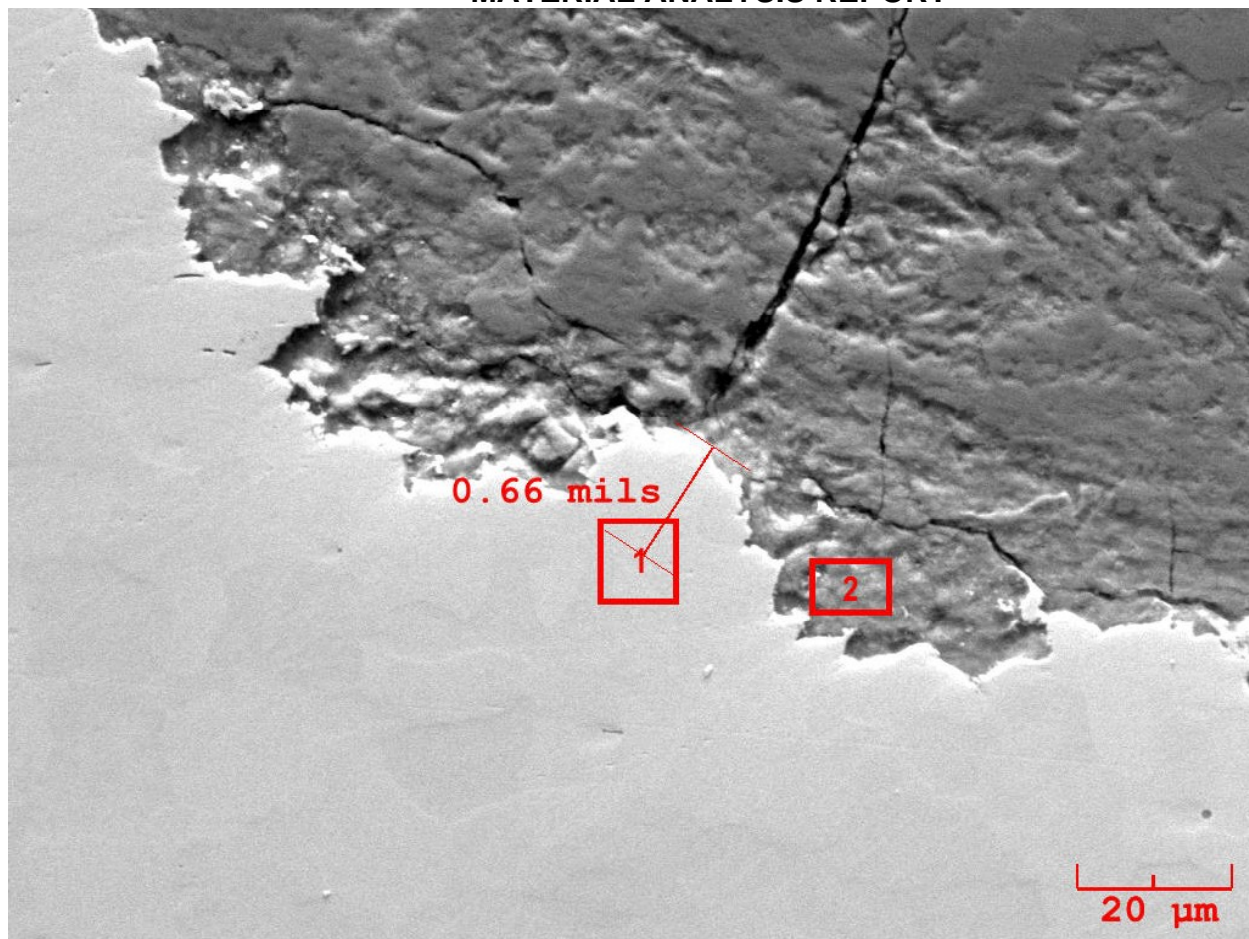


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FIGURE 32, LINER SAMPLE "B", QUADRANT #10, SECTION #3, OD PIT, DETAIL IN THE SEM.

TEST SAMPLE [^]	CHEMICAL COMPOSITION, WT. %												
	O	NA	Mg	AL	SI	S	K	CL	CA	TI	CR	MN	FE
"B", Q10-#3, PIT-1	ND	ND	ND	ND	0.4	ND	ND	ND	ND	ND	ND	0.6	99.0
"B", Q10-#3, PIT-2	18.3	ND	ND	0.9	0.6	ND	0.3	ND	0.2	ND	ND	0.4	79.2

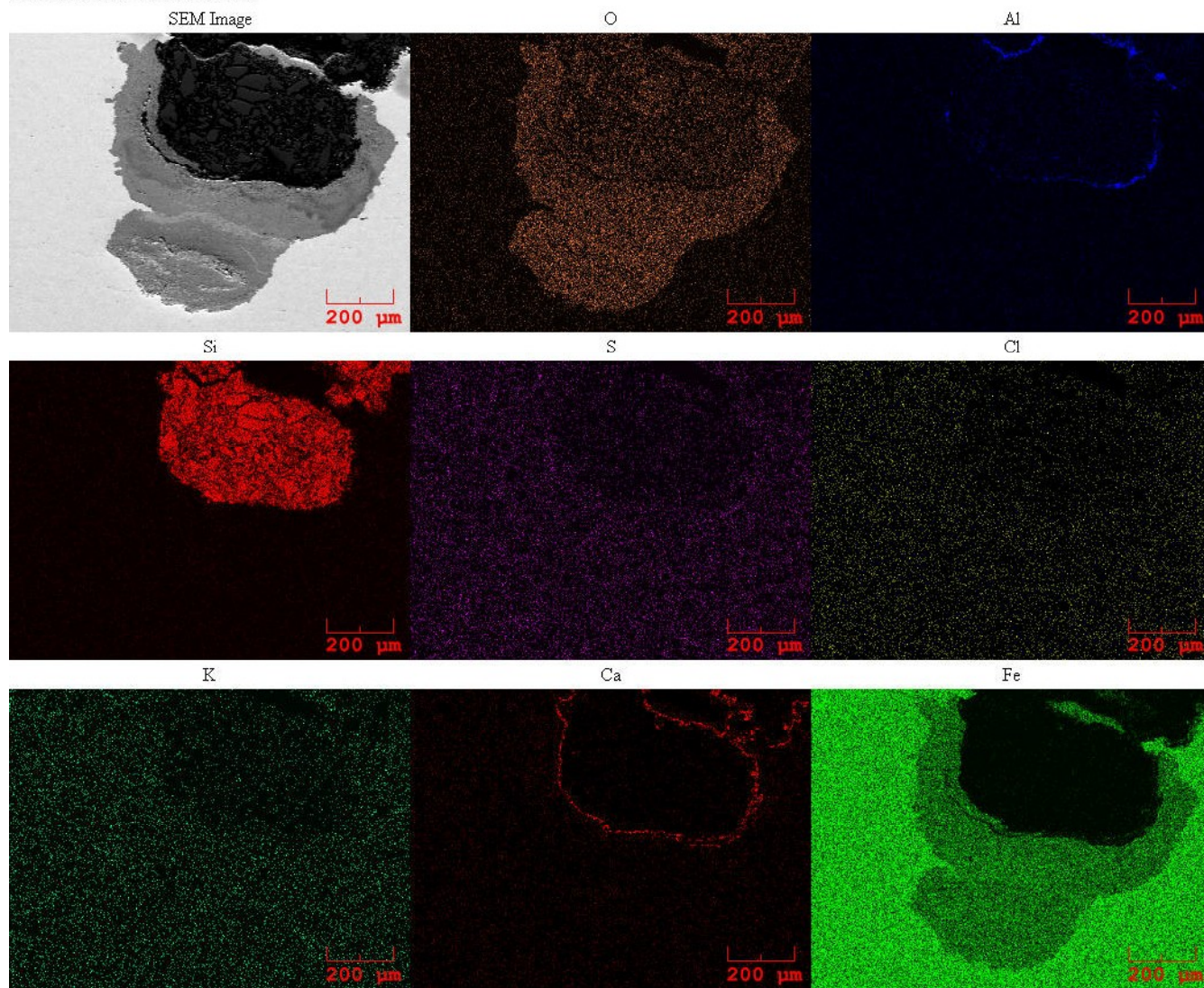
NOTES: *THE SAMPLES WERE REVIEWED UTILIZING SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS). ANY QUANTITATION OF SPECTRA IS CALCULATED BY A STANDARDLESS EDS ANALYSIS PROGRAM. DUE TO THE NATURE OF THE TECHNIQUE ALL VALUES SHOULD BE CONSIDERED APPROXIMATIONS AND "FOR INFORMATION ONLY".

[^]METALLOGRAPHIC SECTIONS, AS-POLISHED WITH ALUMINUM OXIDE. ND = NOT DETECTED.

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Sample B, Q10, #3, Maps at 200x



**FIGURE 33, LINER SAMPLE "B", QUADRANT #10, SECTION #3, OD PIT;
SEM-EDS ELEMENTAL DOT-MAPPING.**

THE MATERIAL FILLING THE BOTTOM OF THIS PIT APPEARS TO BE MAINLY FE AND O.

NOTES: THE SAMPLE HAS BEEN POLISHED WITH ALUMINUM OXIDE.
THE SI SEEN HERE REPRESENTS THE MOLD MATERIAL USED TO ENCAPSULATE THE SAMPLE.

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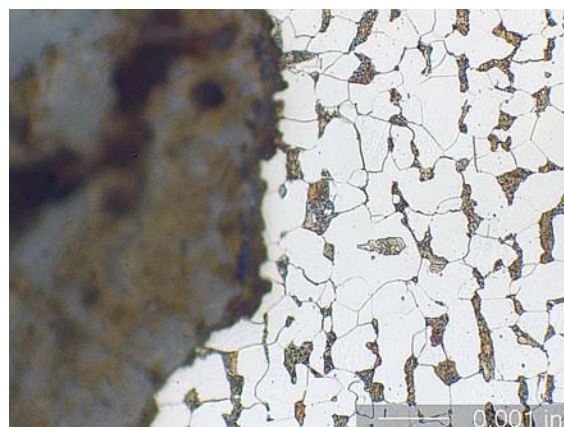
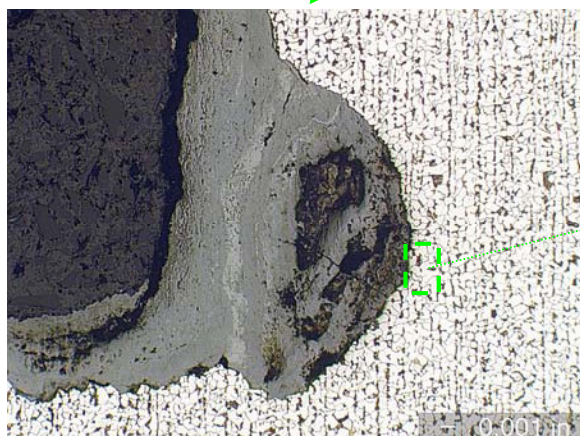
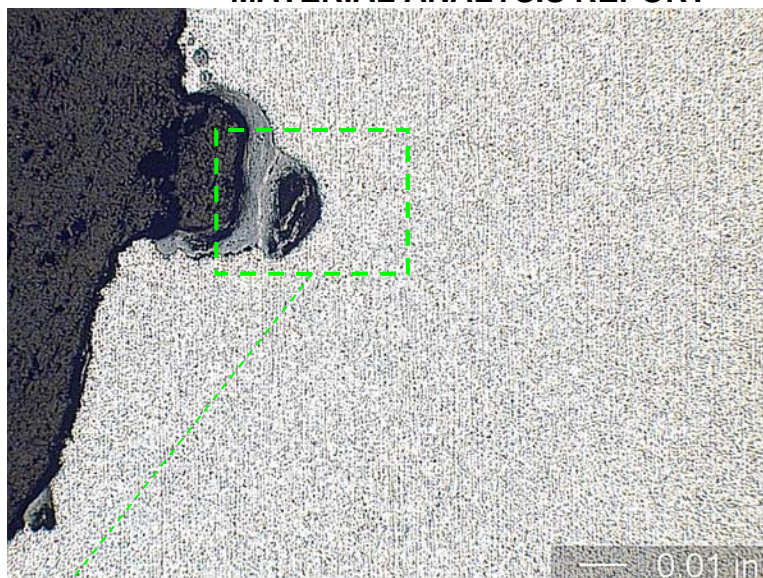
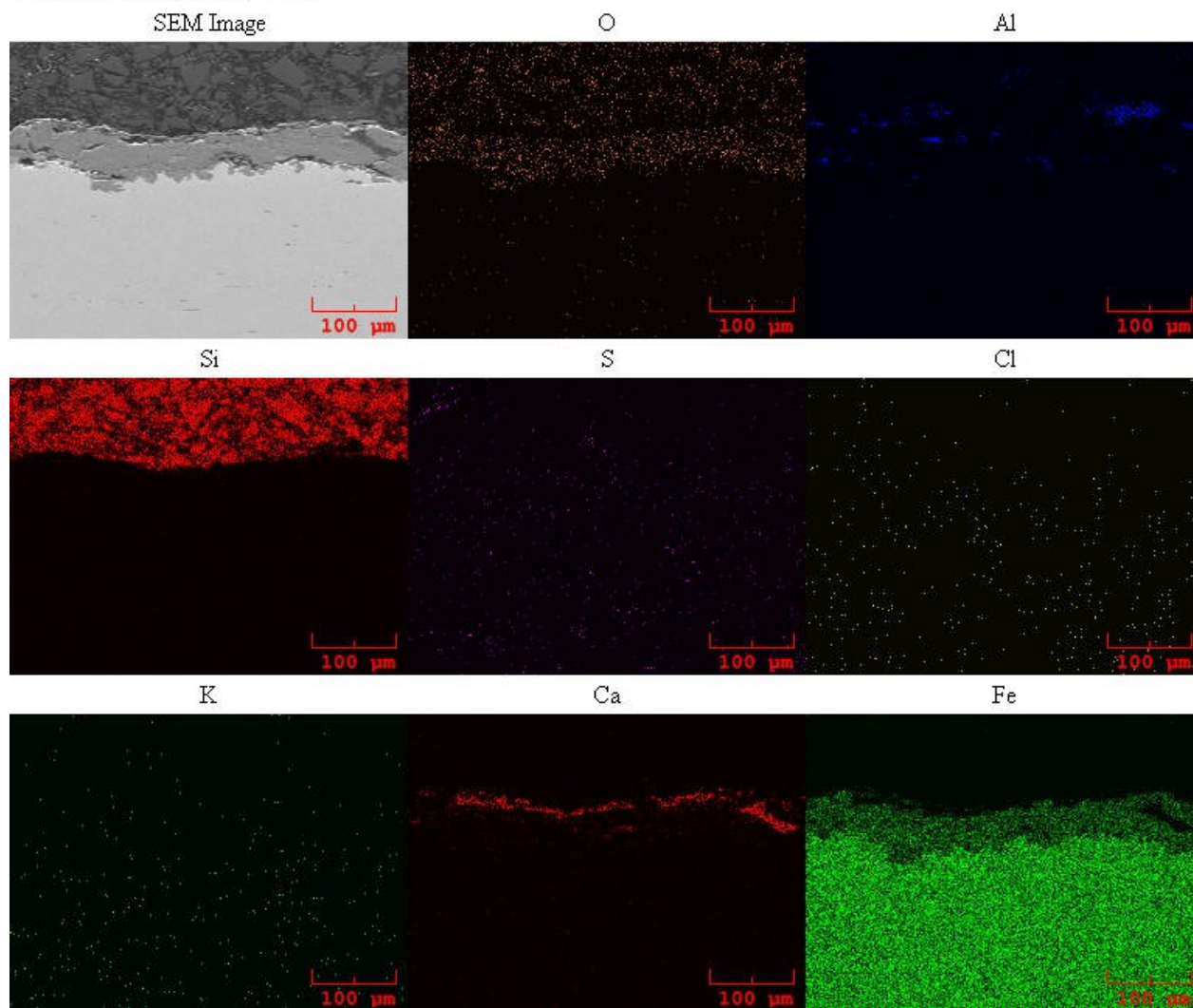


FIGURE 34, LINER SAMPLE "B", QUADRANT #10, SECTION #3, OD PIT MICROSTRUCTURES.

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Mount, AQ11-5, Maps at 500x



**FIGURE 35, LINER SAMPLE "A", QUADRANT #11, SECTION #5;
OD SURFACES IN SECTION, DETAIL IN THE SEM.**

TEST SAMPLE^	CHEMICAL COMPOSITION, WT. %												
	O	NA	Mg	AL	SI	S	K	CL	CA	TI	CR	MN	FE
OD "SCALE"	23.4	ND	ND	0.3	0.7	0.7	ND	ND	2.3	ND	ND	0.4	72.1

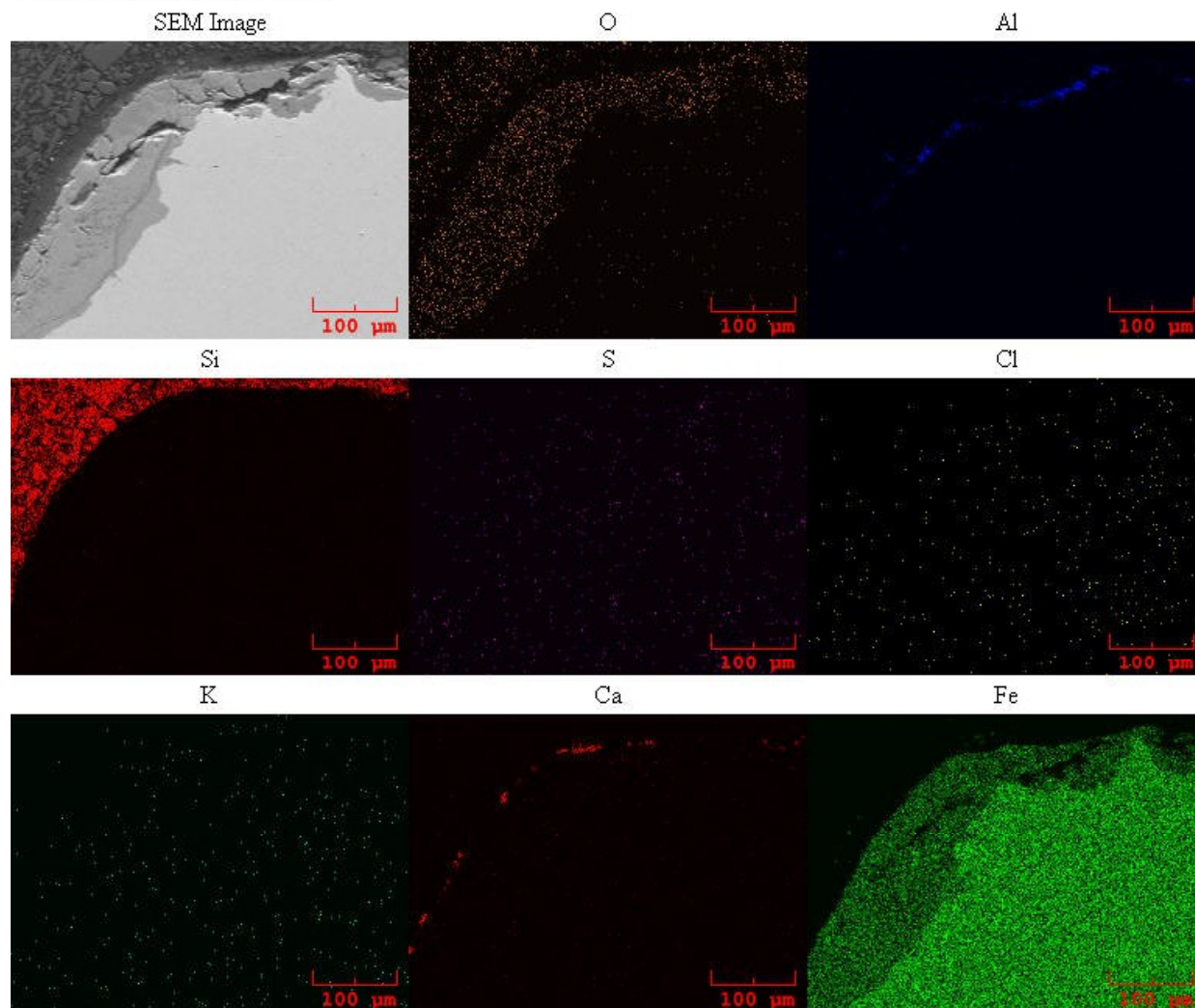
NOTES: *THE SAMPLES WERE REVIEWED UTILIZING SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS). ANY QUANTITATION OF SPECTRA IS CALCULATED BY A STANDARDLESS EDS ANALYSIS PROGRAM. DUE TO THE NATURE OF THE TECHNIQUE ALL VALUES SHOULD BE CONSIDERED APPROXIMATIONS AND "FOR INFORMATION ONLY".

^METALLOGRAPHIC SECTIONS, AS-POLISHED WITH ALUMINUM OXIDE. ND = NOT DETECTED.

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Mount, AQ11-6, Maps 1 at 500x



**FIGURE 36, LINER SAMPLE "A", QUADRANT #11, SECTION #6;
OD SURFACES IN SECTION, DETAIL IN THE SEM**

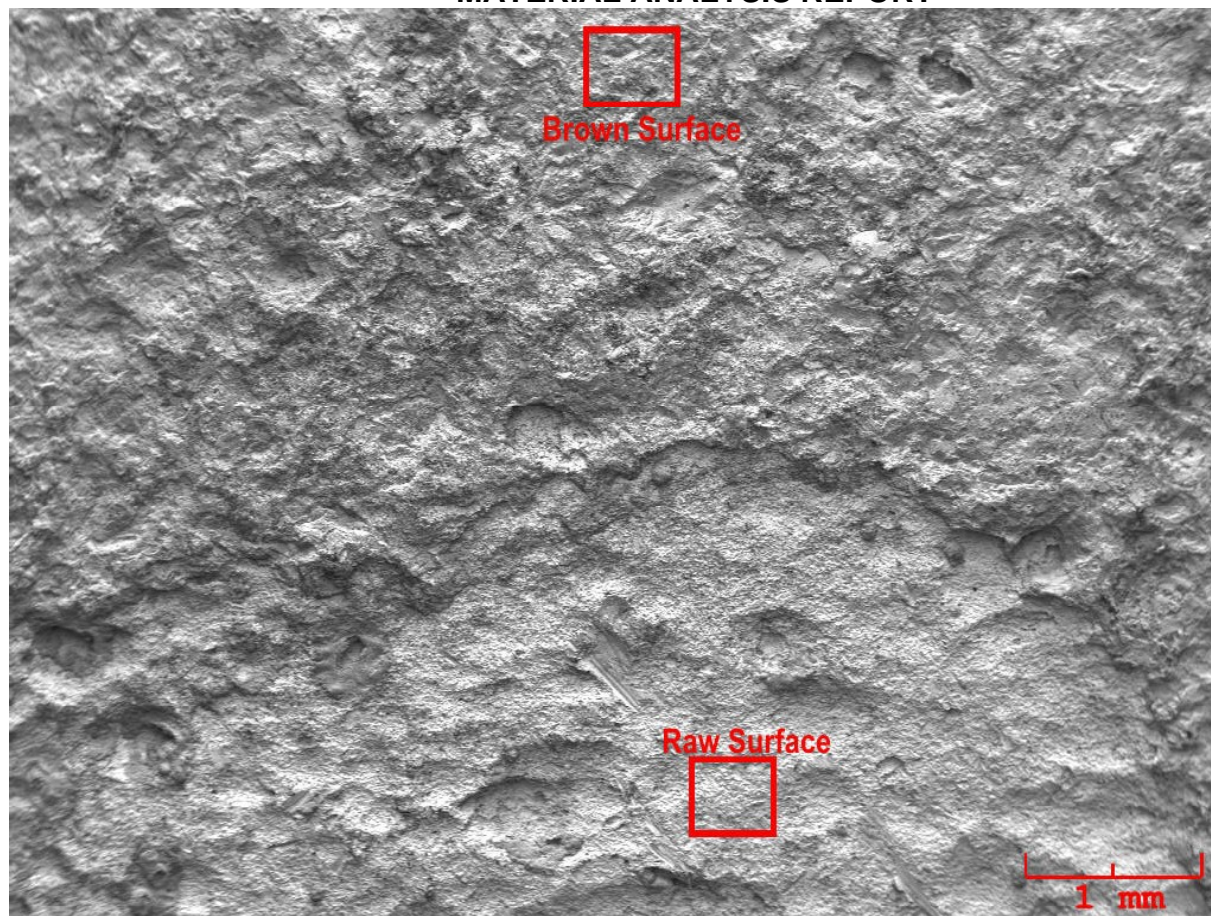
TEST SAMPLE [^]	CHEMICAL COMPOSITION, WT. %												
	O	NA	Mg	AL	SI	S	K	CL	CA	TI	CR	MN	FE
OD "SCALE"	15.9	ND	ND	ND	1.6	ND	ND	ND	0.4	ND	ND	0.5	81.7

NOTES: *THE SAMPLES WERE REVIEWED UTILIZING SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS). ANY QUANTITATION OF SPECTRA IS CALCULATED BY A STANDARDLESS EDS ANALYSIS PROGRAM. DUE TO THE NATURE OF THE TECHNIQUE ALL VALUES SHOULD BE CONSIDERED APPROXIMATIONS AND "FOR INFORMATION ONLY".

[^]METALLOGRAPHIC SECTIONS, AS-POLISHED WITH ALUMINUM OXIDE. ND = NOT DETECTED.

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**FIGURE 37, LINER SAMPLE "A", QUADRANT #11, PIECE IN THE SEM;
IN-SITU OD SURFACES AFTER CLEANING[^].
BOX DETAILS ARE SHOWN BELOW.**

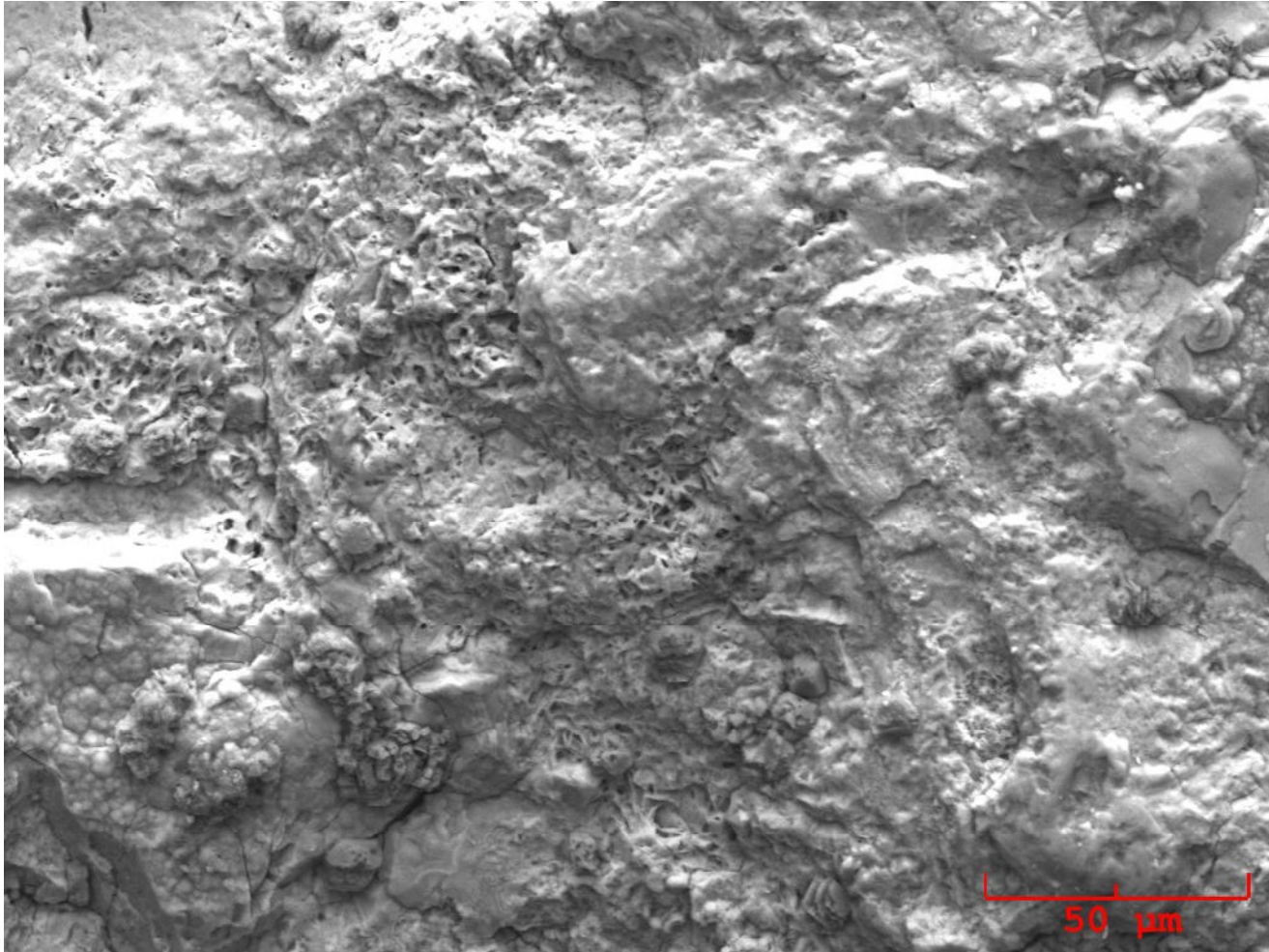
SAMPLE	CHEMICAL COMPOSITION (WT. %) VIA EDS*													
	O	NA	Mg	AL	SI	S	K	CL	CA	TI	CR	MN	FE	ZN
BROWN SURFACE	26.6	ND	ND	0.5	1.4	0.2	ND	ND	5.9	ND	ND	0.6	64.4	0.4
RAW (WHITE) SURFACE	4.2	ND	ND	0.2	0.7	ND	ND	ND	0.2	ND	ND	0.5	94.2	ND

NOTES: [^]ULTRASONICALLY CLEANED IN DE-IONIZED WATER AND LIGHTLY SCRUBBED WITH A SOFT BRUSH.

*THE SAMPLE WAS REVIEWED UTILIZING SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS). ANY QUANTITATION OF SPECTRA IS CALCULATED BY A STANDARDLESS EDS ANALYSIS PROGRAM. DUE TO THE NATURE OF THE TECHNIQUE ALL VALUES SHOULD BE CONSIDERED APPROXIMATIONS AND "FOR INFORMATION ONLY".

ND = NOT DETECTED.

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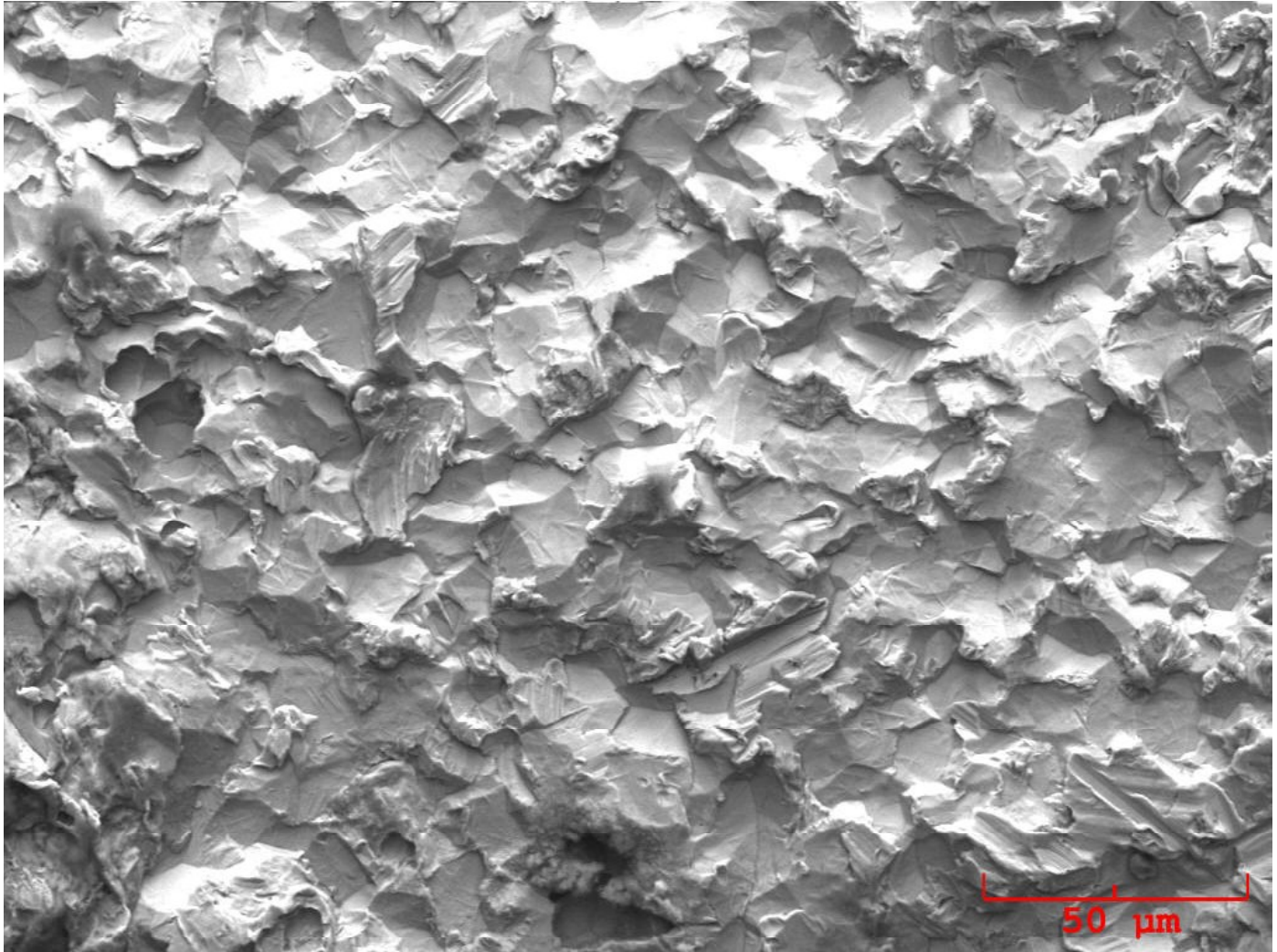
MATERIAL ANALYSIS REPORT

**FIGURE 38, LINER SAMPLE "A", QUADRANT #11, CLEANED PIECE;
BROWN SURFACE DETAIL IN THE SEM.**

THIS SURFACE IS MOSTLY Fe (64.4%), O (26.6%), AND CA (5.9%).

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**FIGURE 39, LINER SAMPLE “A”, QUADRANT #11, CLEANED PIECE;
WHITE SURFACE DETAIL IN THE SEM.**

THIS SURFACE IS MOSTLY Fe (94.2%) AND O (4.2%).

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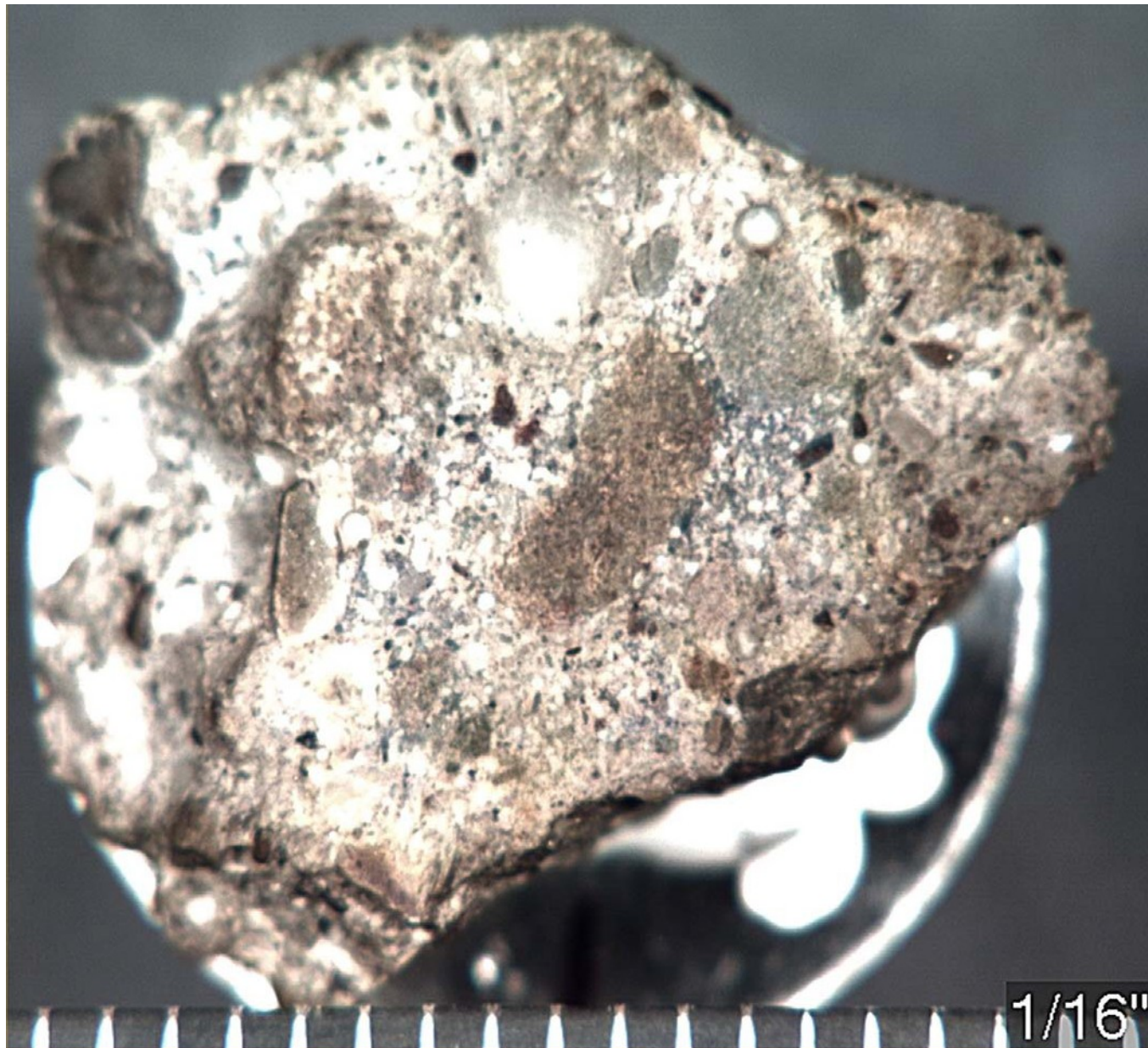
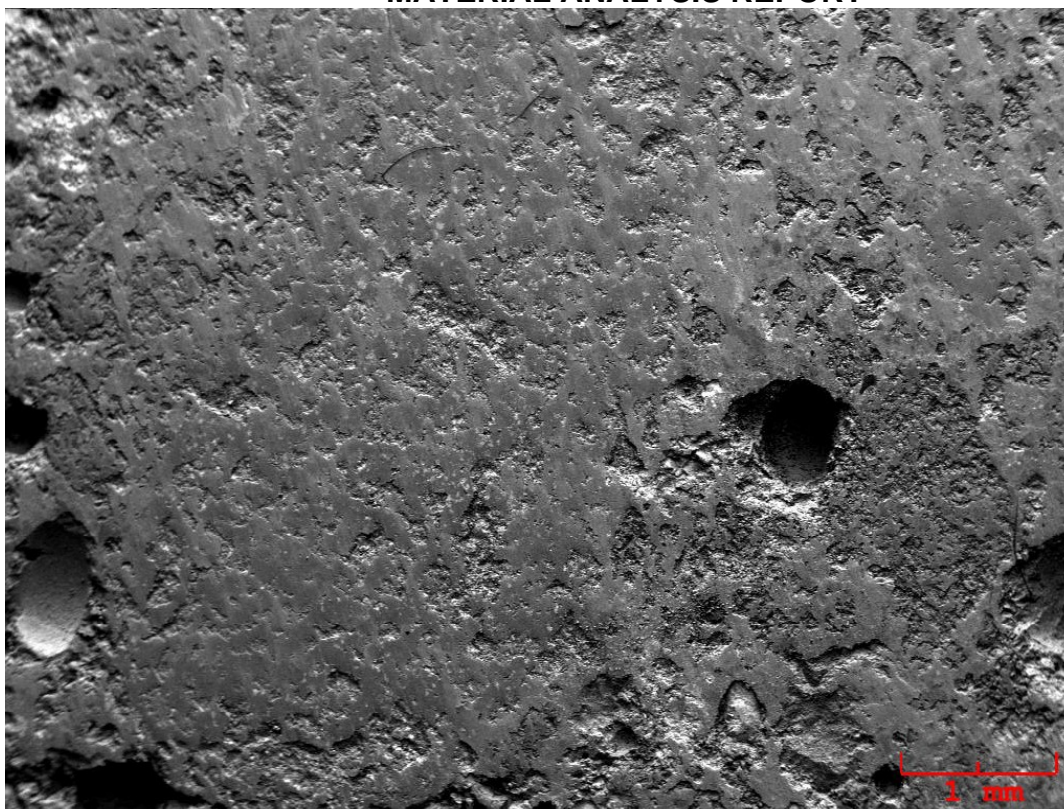
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FIGURE 40, CONCRETE SAMPLE #1, 1ST (“LARGE PIECE”) FOR SEM STUDY.
REMOVED FROM THE BACK (RE-BAR SIDE) AND GROUND FLAT FOR ANALYSIS.

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Concrete, #1, Area A, taken at 35x
SEM Image

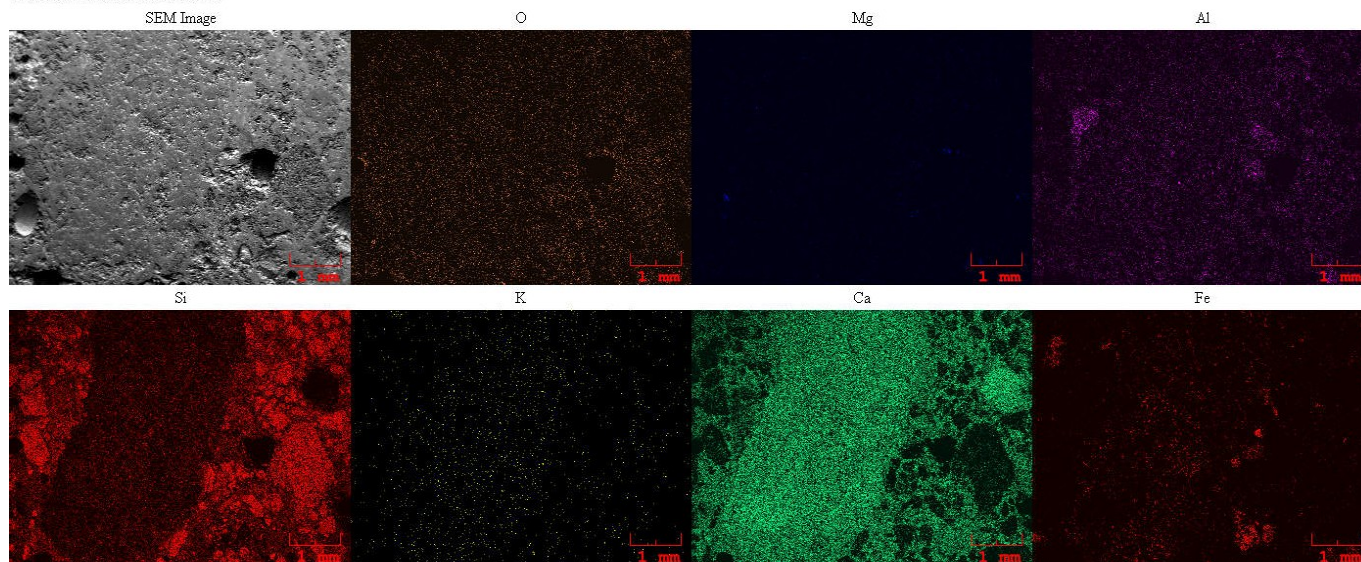


FIGURE 41, CONCRETE SAMPLE #1, 1ST (“LARGE PIECE”), AREA “A” SEM-EDS ELEMENTAL DOT-MAP.

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Concrete, #1, Area B, taken at 35x

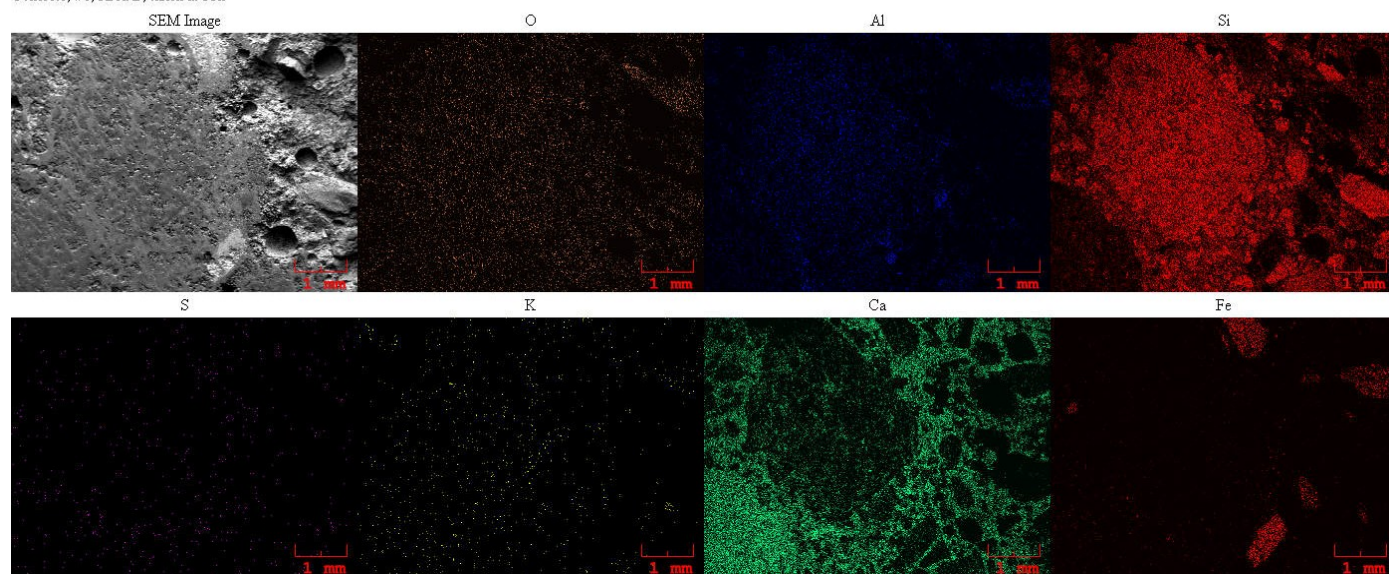


FIGURE 42, CONCRETE SAMPLE #1, 1ST (“LARGE PIECE”), AREA “B” SEM-EDS ELEMENTAL DOT-MAP.

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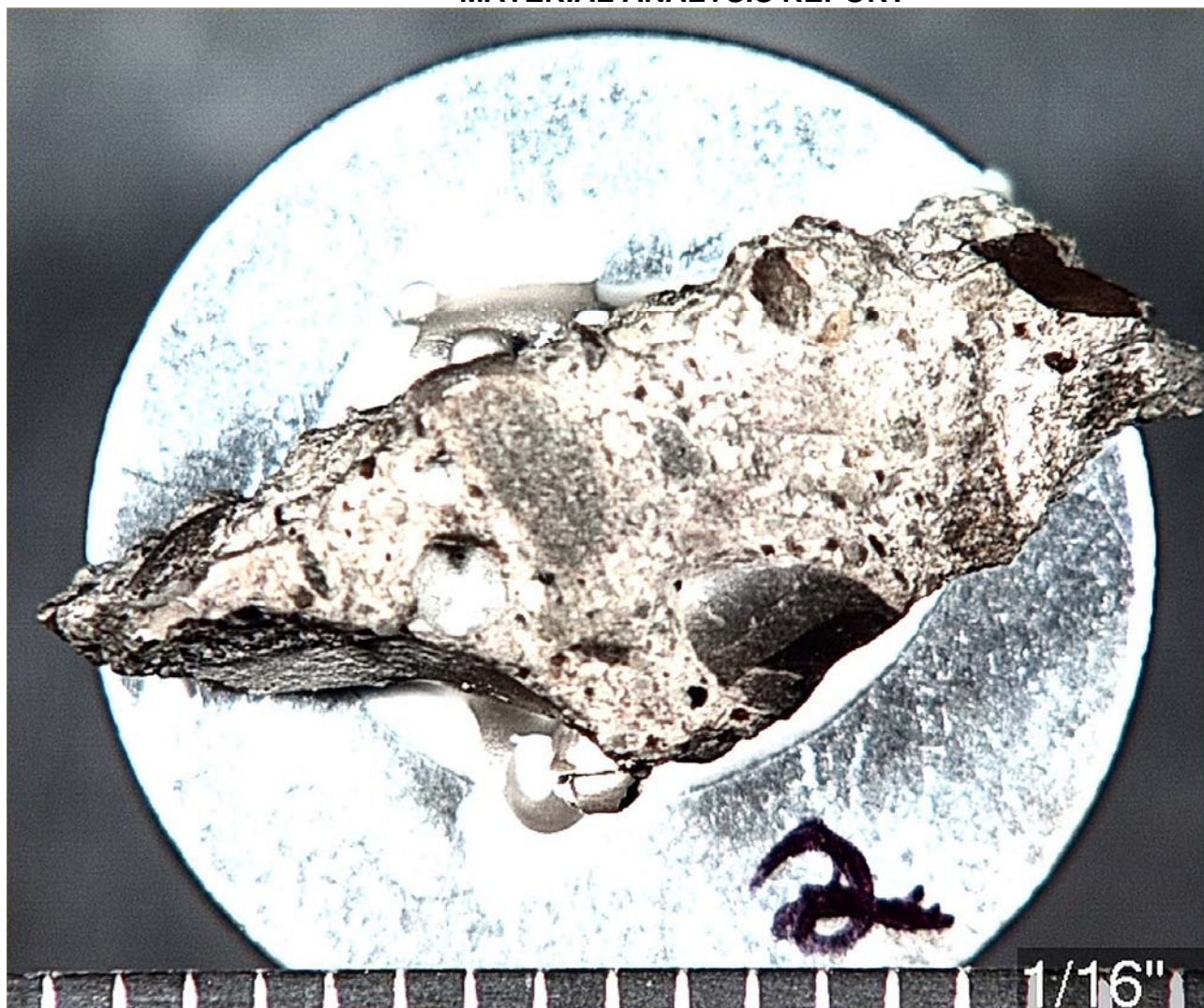


FIGURE 43, CONCRETE SAMPLE #2, “SMALL PIECE” FOR SEM STUDY.
REMOVED FROM THE END OF THE “SMALL PIECE” AND GROUND FLAT FOR ANALYSIS.

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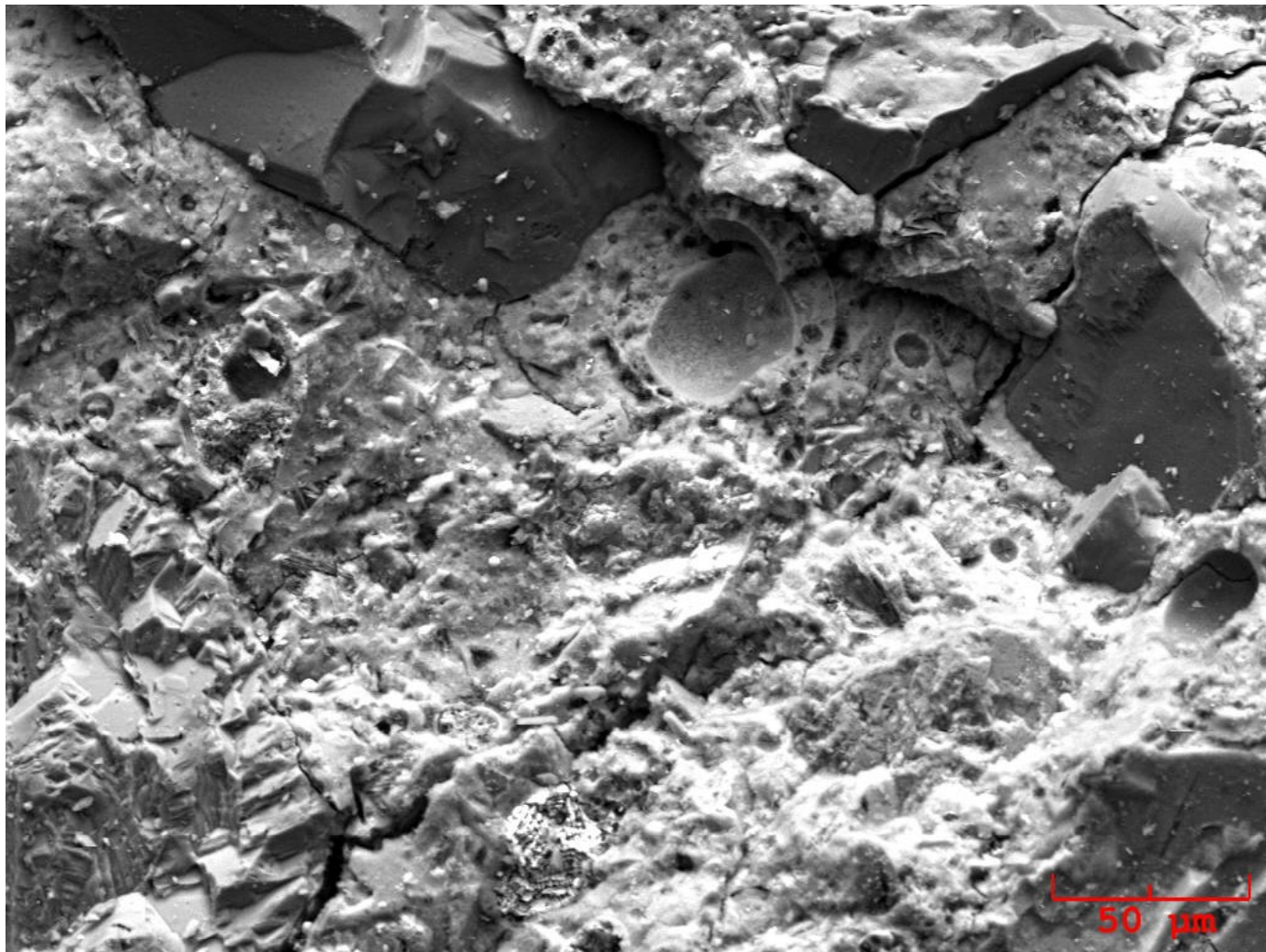
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FIGURE 44, CONCRETE SAMPLE #2, “SMALL PIECE”, AREA “A” DETAIL IN THE SEM.

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Concrete, #2, Area A, Maps at 750x

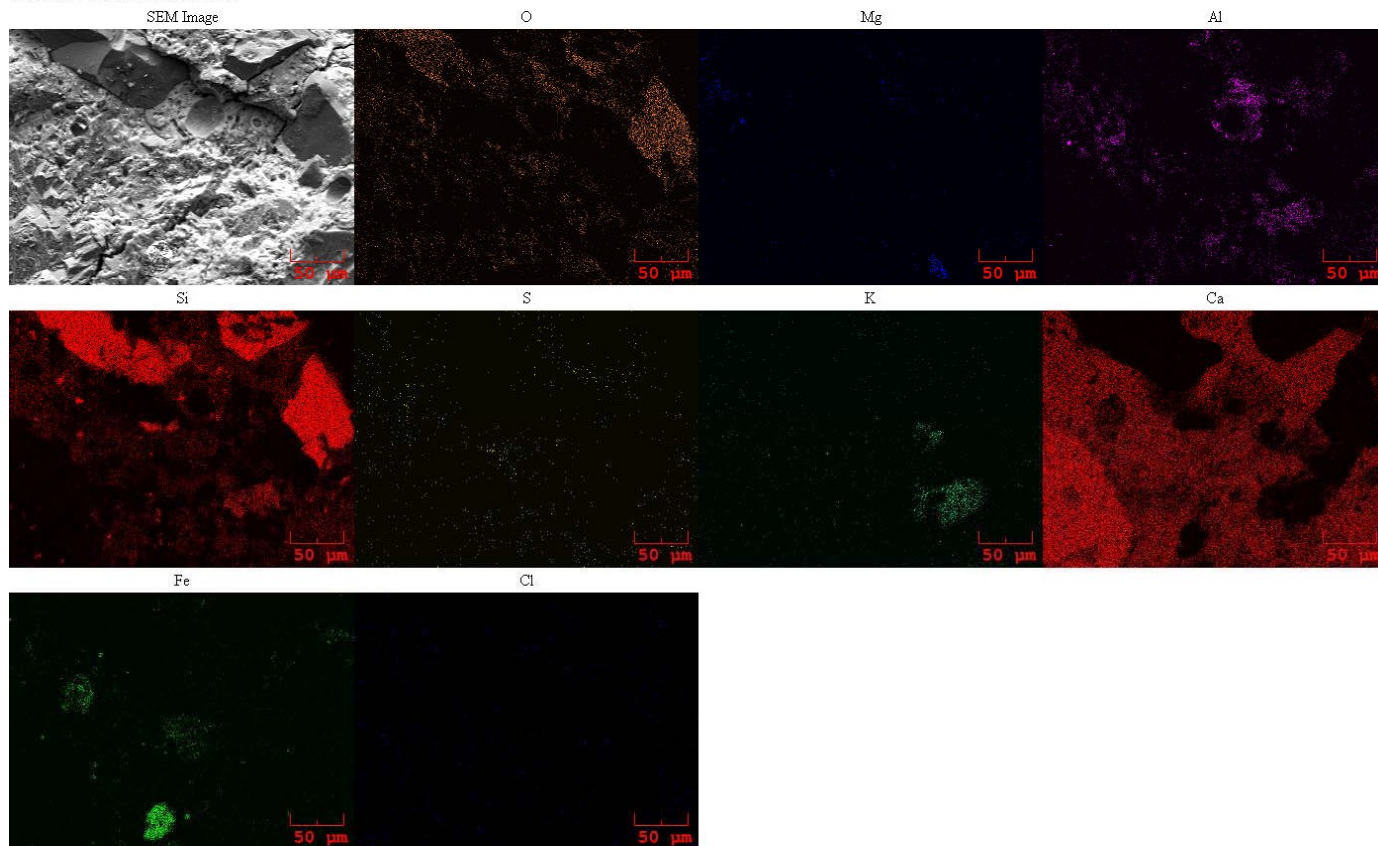


FIGURE 45, CONCRETE SAMPLE #2, “SMALL PIECE”, AREA “A” SEM-EDS ELEMENTAL DOT-MAP.

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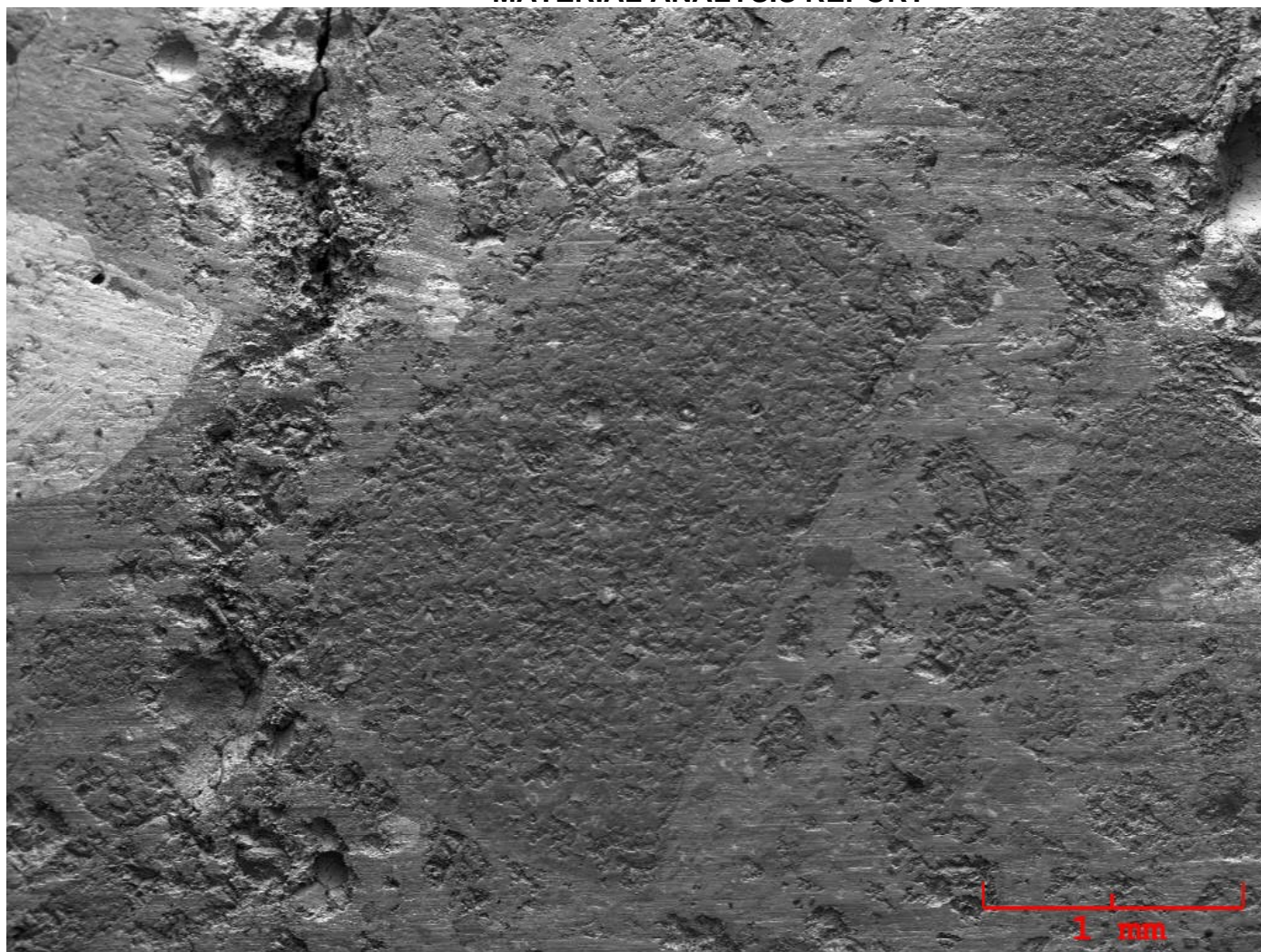
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FIGURE 46, CONCRETE SAMPLE #2, "SMALL PIECE", AREA "B" DETAIL IN THE SEM.

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Concrete, #2, Area B, Maps at 50x

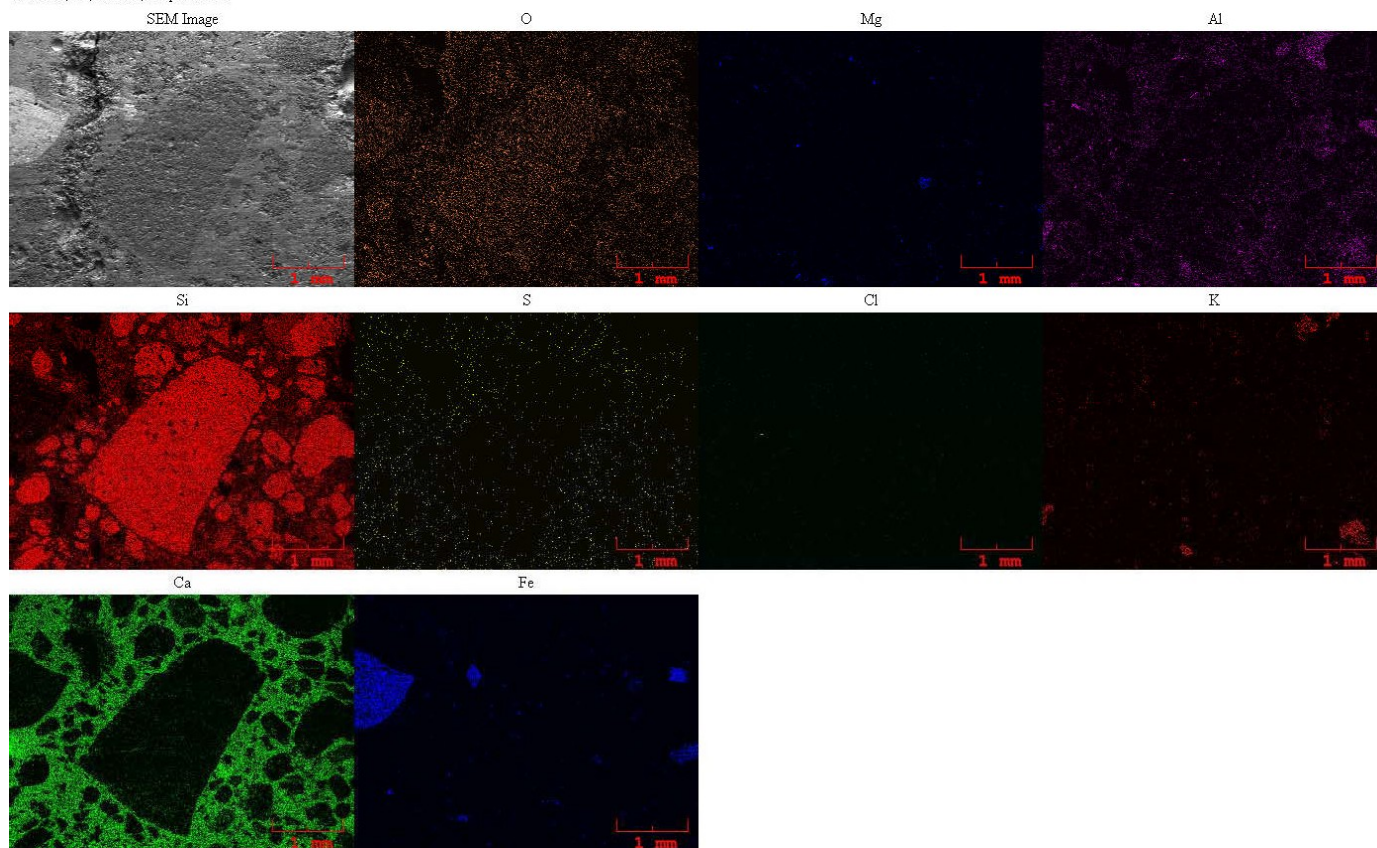


FIGURE 47, CONCRETE SAMPLE #2, “SMALL PIECE”, AREA “B” SEM-EDS ELEMENTAL DOT-MAP.

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MATERIAL ANALYSIS REPORT


FIGURE 48, CONCRETE SAMPLE #1, ("LARGE PIECE"), BROKEN FOR TESTS, AS-MARKED.
NOTE: THE WATER LAB TEST SAMPLE WAS FOR WATER-SOLUBLE CL.

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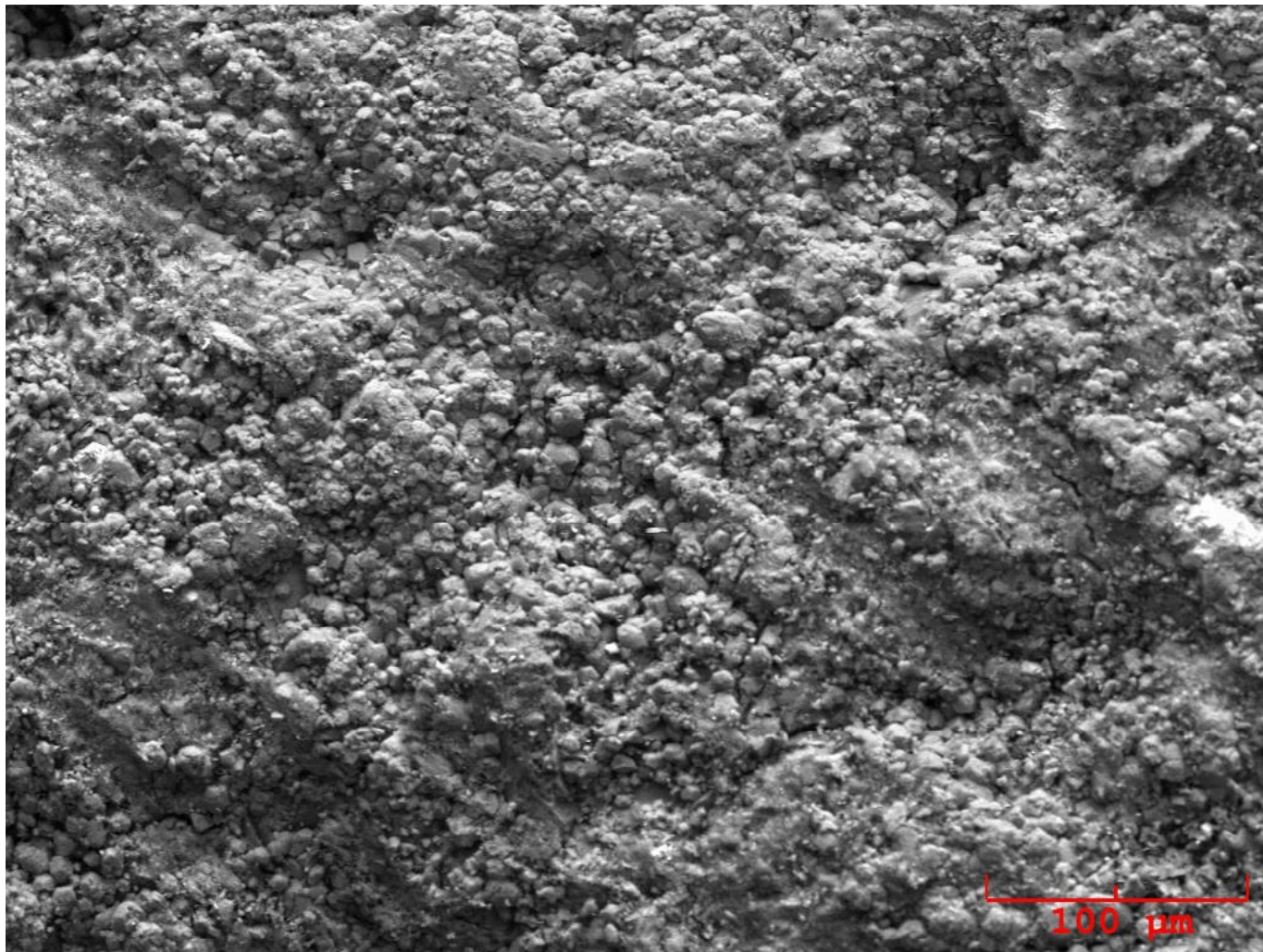


FIGURE 49, LARGE CONCRETE SAMPLE (FROM #1), “FLAT” SURFACE, “SPECIAL”, AS-IS IN THE SEM.

CHEMICAL COMPOSITION (WT. %) VIA EDS*												
O	NA	Mg	AL	SI	S	K	CL	CA	TI	CR	MN	FE
41.0	ND	1.0	2.2	13.6	0.4	0.2	0.1	38.5	ND	ND	ND	2.9

NOTES: REPORTEDLY, THIS SAMPLE HAD TO BE FOAM-CLEANED TO ALLOW ITS RELEASE FROM THE PLANT.

*THE SAMPLE WAS REVIEWED UTILIZING SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS). ANY QUANTITATION OF SPECTRA IS CALCULATED BY A STANDARDLESS EDS ANALYSIS PROGRAM. DUE TO THE NATURE OF THE TECHNIQUE ALL VALUES SHOULD BE CONSIDERED APPROXIMATIONS AND “FOR INFORMATION ONLY”.

ND = NOT DETECTED.

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MATERIAL ANALYSIS REPORT

Attachment #1

TEST EQUIPMENT and PROCEDURES

TEST	INSTRUMENT & MODEL	CALIBRATION DUE DATE	BETA No.	LSS PROCEDURE	
				NUMBER & TITLE	REV No.
Failure Analysis	N/A	N/A	N/A	B0069, Failure Analysis	0
Chemical Analysis	Thermo ARL 3460 Optical Emission Vacuum Spectrometer	Performance check prior to use	BETA 665	B0068, Thermo ARL 3460 Optical Emission Vacuum Spectrometer Analysis	0
Chemical Analysis	Outokumpu Instruments Arc-Met 900, Model 158877	Standardize prior to use	BETA 534	D0037	*
Chemical Analysis – SEM/EDS	Amray Scanning Electron Microscope, Model: 1830T4, S/N: 18321002, with IXRF Energy Dispersive X-ray Spectrometer	*	BETA 386 BETA755	Interim Cover Sheet IXRF Systems EDS2004 Version 1.3 Software User's Guide expiration date 5/31/2006	*
Chemical Analysis – SEM/EDS	Camscan Scanning Electron Microscope, Model: MV2300U, S/N: US0187039/VG0540181U with IXRF Energy Dispersive X-ray Spectrometer and x-ray Optics/AAT Detector	7/16/2006	BETA 602 BETA756	Interim Cover Sheet IXRF Systems EDS2004 Version 1.3 Software User's Guide expiration date 5/31/2006	NA
Rockwell Hardness	Wilson Rockwell 524T Hardness Tester, Model 83259910	Performance check prior to use	BETA 400	D0027, Wilson Rockwell Model 524T Hardness Tester	2
Knoop/Vickers Hardness	Buehler Micromet II Digital Microhardness Tester, Model B-D58222	Performance check prior to use	BETA 401	D0028	*
Field Hardness	Proceq Equotip Hardness Tester, Model 25-819	Performance check prior to use	BETA 428	D0016	*
Field Replication	N/A	N/A	N/A	B0037	*
Reagent Preparation	N/A	N/A	N/A	C0005, Metallurgical Reagents**	1
Sample Remelting	Zeebac Kel-Melt Sample Remelt Furnace, Model S/N KD520470	N/A	BETA259	D0045	*
Linear Measurements by Optical Methods	LECO Inverted Metallograph PMG-3 with MSQ Image Analysis System Program Version 6.5.1	*	BETA419 BETA 754	D0040	*
Average Grain Size	LECO Inverted Metallograph PMG-3 with MSQ Image Analysis System Program Version 6.5.1	*	BETA419 BETA 754	D0039	*
Graphite Classification	LECO Inverted Metallograph PMG-3 with MSQ Image Analysis System Program Version 6.5.1	NA	BETA419 BETA 754	D0041	*
Dimensional	Starrett Micrometer S/N 210-A	*	BETA 168	NA	*
Dimensional	Starrett Vernier S/N 120	*	BETA 166	NA	*
Mass	Mettler AE-100 S/N C-31383	*	BETA 113	NA	*
Mass	Sartorius LP-6200S	Performance check prior to use	MLL0009	NA	*

*Denotes procedures or instruments not used in this report.

**2% Nital.

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MATERIAL ANALYSIS REPORT

Attachment #2,

Water Lab, Water Solubles Concrete Analysis, p. 1 of 2



BETA Laboratory
ISO 9001 Registered

File No. 06-00090

BETA Laboratory

Chemical Analysis

6670 Beta Dr., Mayfield Village OH 44143 (440)-604-9832

TO David Klesch

MAIL STOP A-BETA

FROM J. L. Hirsch DATE 3/3/06
PHONE 824-9832 MAIL STOP BETA
SUBJECT Analysis of BVPS Concrete for pH & Chloride

Requisition No.: 14890
Beta Metallurgical Sample ID #: M06074
Date Received: 3/2/06
Date Completed: 3/3/06

Results:

Sample Identification	% Water Soluble	pH @ temp	Chloride in ppm
Large Piece #1 flat surface	2.58 %	10.62 @ 21.1 deg C	0 ppm
Small Piece #2	2.59 %	10.67 @ 20.7 deg C	0.56 ppm

Discussion:

The two samples of concrete were crushed in a vice and passed through a #20 sieve. Approximately 3 grams of the powder was placed in 200 ml of deionized water at room temperature for 18 hours. The solutions were then passed through a glass fritted Millipore vacuum filtration system. The solid material left behind in the filter was dried and weighed for determination of the % water soluble. The liquid sample volume was elevated to 250 ml with the addition of deionized water. The pH of both samples was taken then they were run on the ion chromatograph to determine chloride content.

Equipment:

Thermo Orion Model EA940 (pH meter), BETA 585, calibrate before use

Dionex Ion Chromatograph, BETA 342-344

Mettler Toledo Balance Model AG104, BETA 610, calibrate before use
Balance Weight set, BETA 479

Analysis Performed By J. L. Hirsch 3-3-06

Reviewed By T. D. Smith Date 3-3-06

Approved By [Signature] Date 3/3/06

cc:\ J. Blough

Attachment: Intralaboratory Chain of Custody

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MATERIAL ANALYSIS REPORT

Attachment #2

Water Lab, Water Solubles Concrete Analysis, p. 2 of 2

BETA LABORATORY
INTRALABORATORY CHAIN-OF-CUSTODY FORM

FROM: ☐ Coal ☐ Fuel Oil ☐ Oil ☐ Water ☐ Field ☐ CMID ☒ Metallurgy ☐ Metrology ☐ Fire ☐ C&MT
(Sending Lab) (Check One)

TO: ☐ Coal ☐ Fuel Oil ☐ Oil ☒ Water ☐ Field ☐ CMID ☐ Metallurgy ☐ Metrology ☐ Fire ☐ C&MT
(Receiving Lab) (Check One)

DESIRED TURN-AROUND-TIME: ASAP

[illegible]

CMID = Chemical Materials Identification; C&MT = Component & Material Test

PC-133 (10-21-04)

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Attachment 9

Beaver Valley Report by Eldon Dille

(63 pages)

Draft

Beaver Valley Unit 1
Engineering Assessment Report
1 R 17 Exterior Containment Liner Corrosion

Prepared for FirstEnergy Corp.

Eldon R. Dille

March 2006

Draft

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PROBABLE FUTURE CORROSION	

Draft

EXECUTIVE SUMMARY

The Beaver Valley Unit 1 is a pressurized water nuclear reactor located at Shippingport, PA. The containment cylinder is composed of a nominal 3/8-inch thick carbon steel inner liner and a carbon steel reinforced concrete outer shell.

During the process of cutting an approximately 17 1/2-foot by 20-foot opening through the containment vessel/steel liner three localized areas of corrosion were found. The three areas totaled about 4 square feet of area. A photographic record was made of the carbon steel liner cutout. A corrosion consultant was retained to evaluate the discovered corrosion. This engineering evaluation is the results of his effort.

Two of the corroded areas were removed from the 17 1/2-foot by 20-foot cutout and sent to Beta Laboratory for detailed metallurgical and chemical analysis of corrosion areas and possible remaining corrosion products. Since the corroded areas had been cleaned by water blasting during the construction removal work, only minimal corrosion products remained in/or on the corroded samples.

The existing condition of the containment vessel was assessed by performing various examinations and laboratory analysis. Provided below is a summary of these examinations and laboratory analyses and the conclusions reached therefrom:

- The containment vessel wall thickness in the corrosion-affected areas was determined by performing Ultrasonic Testing (UT) measurements. Evaluation of the UT measurements revealed that a reduction in the specified nominal wall thickness of 3/8-inch of the containment liner had only occurred in a few locations, thus a localized condition. One pit with a remaining wall thickness of 0.151-inch was measured in Area 2. In Area 1 a remaining wall thickness of 0.225-inch was measured in a very small pit. The photographs reveal some of the original mill scale is remaining on the cutout panel where it was not removed by water blasting.
- Metallurgical analyses of the cutout panel revealed a metallurgical analysis of a typical 0.19% carbon silicon killed steel with a hardness range of 71.3 to 76.5 HRB.
- Laboratory analyses, including scanning electron microscope analyses for potential corrosion products, were used on the corroded steel samples. The semi-quantitative analyses in the corroded portion of the samples measured up to 26.5% calcium, up to 3.7% silicon, up to 2.9% sulfur and up to 0.3% chlorine.
- Laboratory analyses, including scanning electron microscope analysis for potential corrosion products, were used on two concrete samples. Sample 1 was next to the steel liner and Sample 2 was about half way through the concrete cover over the containment liner. The semi-quantitative analyses

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of the concrete samples revealed: 20.2% to 38.5% calcium, 13.6% to 33.8% silicon, 0.3% to 0.4% sulfur. In Sample 1, no water leachable chlorides were found and the pH of the concrete was 10.62. In Sample 2, 0.56 PPM of water leachable chlorides were found and the pH of the concrete was 10.67.

- Results of laboratory analyses confirmed the type of corrosion mechanism identified by visual examination: oxygen concentration cell corrosion on the corroded areas of the 17 1/2-foot by 20-foot containment liner cutout. One analysis on the surface of a corrosion pit indicated up to 0.3% chloride on the surface of a corrosion pit indicates a possible present of sufficient chlorides to contribute to an auto-catalytic corrosion of steel.
- The majority of the cutout panel (about 99%) had experienced only minimal corrosion. Most of the original mill scale was still present on the steel when the concrete was removed from the cutout by water blasting. (This observation is based on the fact that there is mill scale present on the steel adjacent to the studs attached to the cutout panel).

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1. PURPOSE

This report provides an evaluation and assessment of the corrosion issue and data associated with corrosion of the Beaver Valley Unit 1 containment liner. The Beaver Valley Discovery and Action Plans are defined in CR 06-01122.

The Discovery Action Plan defined the necessary activities to discover, evaluate and assess the probable cause and extent of condition of corrosion on the containment liner (external). This report summarizes the discovery activities and the resulting evaluation and assessment of the “as-found” condition and laboratory results provided per Beta Labs in their report.

This report is an input to the Implementation Action Plan defined in CR 06-01122 for the resolution of the outstanding issues associated with the containment liner corrosion indications. Recommendations are provided in this report for the control of the observed corrosion.

2. BACKGROUND

The Beaver Valley Unit 1 is a Westinghouse pressurized water reactor plant located at Shippingport, PA, that began commercial operation in 1976. The containment vessel is lined with a carbon steel liner fabricated of a nominal 3/8-inch-thick steel plate. The structural containment vessel outside the carbon steel liner plate is fabricated of steel-reinforced concrete.

In February 2006, a portion of the containment carbon steel liner was removed in order to provide an access through the containment vessel for the removal and replacement of the steam generators and reactor vessel head. The containment liner and attached concrete was removed by the use of water blasting cutting technique. When the concrete was removed from the outside of the section to be removed of the containment steel liner, three areas of corrosion were discovered on the exterior surface of the carbon steel liner section. The original corrosion products appear to have been removed from the containment liner steel as the result of the water blasting cutting technique.

Condition reports and inspection activities were initiated resulting in recommendation for further evaluation. The condition report recommended the evaluation of the exterior corroded areas of the removed containment liner section. In support of the overall effort to evaluate the corrosion found on the containment liner plate, a corrosion consultant was contracted in cooperation with Beaver Valley Engineering Staff to perform evaluation, and assessment of the existing and potential for future corrosion of the containment vessel that was discovered in the region of the access area and elsewhere.

3. SCOPE OF WORK

The scope of work contained in this report is:

1. Overall “as-found” assessment of the liner plate corrosion area. This assessment should:
 - a. Description of the “as-found” condition describing the physical nature of the entire surface of the Liner cutout (~ 20 ft by 20 ft) in general noting any corroded areas and their approximate size. Include an assessment of the photographs provided by FENOC of the area prior to your arrival on-site and your visual observations of the piece.
 - b. If possible, provide initial statements of fact regarding the corrosion areas found on the Liner Plate cutout in terms of color of the deposits, morphology of the area of corrosion. This should include statements identifying that the areas of corrosion are indicative of a localized corrosion mechanism, general corrosion mechanism or indeterminate (provide appropriate supportive references for statements of fact).
2. Discussion and integration of the laboratory results of the samples removed. This assessment should provide:
 - a. Technical evaluation of the results of the destructive testing results done by Beta Lab addressing the material microstructures and pit morphology.
 - b. Technical evaluation of the corrosion product analysis and analysis of base metal corrosion front interface, as it relates to a potential corrosion mechanism in the areas of concern.
 - c. Technical evaluation of the analysis provided by the concrete samples taken from the containment wall.
3. Conclusions and Evaluation.
 - a. Discussion of a basis for evidence of local corrosion or general corrosion across the entire liner plate based upon the findings of 1 and 2 above.
 - b. Overall assessment of identifying most likely corrosion mechanism.
 - c. Recommended additional investigations

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- d. Appropriate references shall be provided to support conclusions or otherwise note as professional opinion.

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4. OVERALL “AS FOUND” ASSESSMENT

- 4.1 Description of the “as-found” condition describing the physical nature of the entire surface of the Liner cutout (~ 20 ft by 20 ft) in general noting any corroded areas and their approximate size. Include an assessment of the photographs provided by FENOC of the area prior to your arrival on-site and your visual observations of the piece.
- 4.1.1 The Liner cutout was in the plant yard covered by a plastic tarp. A white tarp was removed from above the two areas where the majority of the corrosion had occurred and a visual inspection of those two areas was made by the author. The corroded areas had the physical appearance of iron rust (iron III oxide, hematite). Each of the two areas was about 2 sq. ft in area. The total corroded area was about 1 % of the Liner cutout. The pitting had the appearance of localized oxygen concentration cell corrosion. Surrounding the pitted areas, mill scale was still attached to the Liner cutout. In addition, the steel studs attached to portions of the Liner cutout showed no evidence of corrosion. Upon making a visual inspection of the Liner cutout, it appeared that all of the original corrosion products appeared to have been removed by the water blasting that was used to remove the concrete from the outside of the Liner cutout.

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4.2 Assessment of FENOC Photographs



Photograph 1. An overall photograph showing the liner before it was removed from the containment. Laboratory Sample 1 is located just left of the center of the plate, just below the middle of the plate and is identified as "AREA 1." Laboratory Sample 2 is located near the right edge of the plate, approximately $\frac{1}{3}$ rd of the distance up the plate and is identified as "AREA 2". Area 3 is located at the upper left-hand corner of the plate and is within the oblong area outlined in white. Area 3 was not removed from the plate because the degree of pitting is much less than on the samples from Area 1 and Area 2, and a lifting lug had been welded in the vicinity of the corrosion.

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Photograph 2. This is a wide angle view showing the location of AREA 1. Note the pattern of undisturbed mill scale in the photograph. It appears as if the original mill scale was removed by water blasting during the process of removing the concrete from the containment liner.

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Photograph 3. This is a close-up view of AREA 1 that includes the entire corroded area. Note the original mill scale shown in the left and right portions of the photograph. Note the original scale throughout the pitted area.

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Photograph 4. This is a wide angle view showing the location of AREA 2. Note the reinforcing bars in the right portion of the photograph that show no visible evidence of rusting.

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Photograph 5. This is a close-up view of AREA 2 that includes the entire corroded area. Note the corroded area includes a portion of a vertical weld. No preferential corrosion has occurred in the heat affected zone of the weld and/or on the weld.

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Photograph 6. Note the sound concrete that is on the left side of the access area. Note the lack of rusting on the reinforcing bars shown in the photograph.

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4.3 Assessment of Consultant Photographs

- 4.3.1 These photographs were taken of two sections of the containment liner plate that displayed corrosion while the plate was located near where it had been removed from containment. The two corroded areas studied contained about a total of 3 to 4 square feet of corroded steel of a 400 square foot removed panel of the steel containment liner.



Photograph 7. Oxygen Concentration Cell Corrosion. Note the attached studs are free of corrosion other than a flash rusting. Note mill scale is present on the steel panel in the upper right portion of the photograph.

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Photograph 8. Note Groove in Center of Photograph. Original mill scale is evident in this photograph in the upper portion of the photograph. There may be some black corrosion products in two of the pits near the center of this photograph.

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Photograph 9. Note Original Mill Scale in Lower Right of Photograph. There is a darkening of the corroded steel in the center of the photograph. (This darkening may have been water coming from pits in the steel as the discoloration was not apparent when the samples were observed in the laboratory). Note no apparent rusting on the steel studs (other than a flash rusting) attached to the corroded plate.

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Photograph 10. Typical of Oxygen Cell Corrosion of Carbon Steel. Note the discoloration surrounding some of the pitted areas. Some original mill scale remains near the corroded areas.

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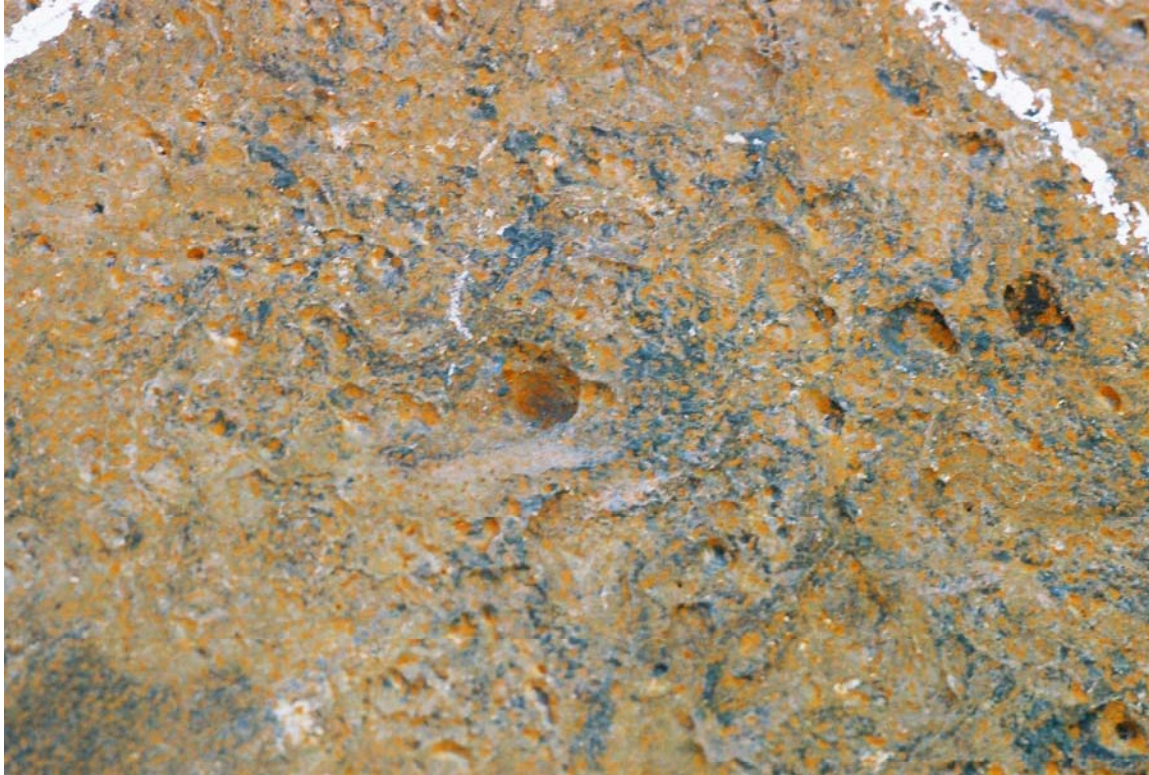
Photograph 11. Deep Depression in Corroded Carbon Steel. Oxygen cell corrosion on the steel panel in addition to the presence of original mill scale. There is a pit within the deep depression.

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Photograph 12. Oxygen Concentration Cell Corrosion. Some mill scale appears throughout the photograph.

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Photograph 13. Localized Pitting Corrosion. Typical of oxygen concentration cell Corrosion. The corrosion pattern has the appearance of having started at several breaks in the original mill scale and then have proceeded over the remainder of the surface in the photograph.

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Photograph 14. Deep Corrosion Channel in Carbon Steel.

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Photograph 15. Details of Corrosion Pit in Carbon Steel.

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- 4.4 If possible, provide initial statements of fact regarding the corrosion areas found on the Liner Plate cutout in terms of color of the deposits, morphology of the area of corrosion. This should include statements identifying that the areas of corrosion are indicative of a localized corrosion mechanism, general corrosion mechanism or indeterminate (provide appropriate supportive references for statements of fact).
- 4.4.1 Visual inspection of the two corroded portions of the Liner cutout revealed what appears to be oxygen concentration cell corrosion of steel. (This is based on the fact that the only colored deposits on the surface of the corroded areas had the visual appearance of iron rust). This corrosion is the result of the steel panel reacting with water and oxygen to form a wide range of iron hydroxides (iron II oxide, iron II hydroxide, and iron III hydroxide) and iron oxides compounds (iron III oxide/iron II oxide, magnetite, etc). The final compound that is usually formed is iron III oxide, hematite.
- 4.4.2 The surface of the Liner plate would have been originally covered by a layer of mill scale. (Mill scale is the layer of iron oxides that forms on the surface of the steel plate as the result of hot rolling. The mill scale is not continuous and exposes the underlying steel to the environment at discontinuities or defects in the mill scale. It is a mixture of three superimposed layer of iron oxides in progressively higher states of oxidation from the metal side outward, viz. iron II oxide (FeO) on the inside, magnetite (Fe₃O₄) in the middle and iron III oxide (Fe₂O₃) on the outside. The relative portions of the three oxides vary with the rolling temperatures. A typical mill scale on 9.5 mm mild steel plate would be about 50 µm thick, and contain approximately 70% FeO, 20% Fe₂O₃, and 10% Fe₂O₃).⁴⁶ In areas where this mill scale was broken, pitting corrosion of the unprotected steel would have begun. The iron III oxide would have formed as the oxygen concentration cell corrosion proceeded where the mill scale was broken. This iron III oxide occupies 7 to 10 times the volume of the uncorroded steel volume. As a result of the increase in the volume of iron III oxides, there would have been pressure between the steel liner and the concrete containment cover.

The initial corrosion of the steel Liner plate likely originated at breaks in the original mill scale. Where these breaks occurred, an anodic corrosion cell would have formed when oxygen and water were also present. Since the initial break (an anodic area) in the original mill scale may have been small (and have been surrounded by a large area of mill scale (cathodic area), a pit would have formed at this location. As the corrosion proceeded, the anodic area would have increased and thus, the pitting corrosion would have began to change to general corrosion (a uniform loss of steel over the corroding area) from the initial localized pitting corrosion (See Table 2).

The areas where the corrosion is observed on the Liner cutouts may not have been in intimate contact with the original concrete. (Laboratory observations by Beta Laboratory found that there were small voids where pockets of air in the concrete

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sample may have existed where the concrete contacts with the steel Liner). This lack of contact between the steel and the concrete could have resulted from the presence of entrained air bubbles, a rag, a piece of wood, or non-tamped concrete. As water came through the concrete and entered the void next to the Liner cutout, oxygen concentration cell corrosion (rusting) of the steel would have begun in these air pocket areas. This corrosion would have continued until the available oxygen was consumed or the water was consumed. If the steel Liner cutout alternated between wet and dry, the probable corrosion rate on the steel would have likely to have increased over the corrosion rate that would have occurred if the steel had been wet all the time

See Appendix A for a technical discussion of the corrosion of steel by water and oxygen.

5.0 DISCUSSION AND INTEGRATION OF THE LABORATORY RESULTS OF THE SAMPLES REMOVED. THIS ASSESSMENT SHOULD PROVIDE:

- 5.1 Technical evaluation of the results of the destructive testing results done by Beta Lab addressing the material microstructures and pit morphology.
 - The metallurgical analysis performed by Beta Laboratory of these selected corroded steel samples indicated the steel has the expected metallurgical composition.
 - The cold working on the interior surface of the steel samples would be consistent with the abrasive blasting that was performed in order to secure a good surface for proper paint adhesion.
 - No significant cold working was found on the external surfaces of the steel containment liner samples. Therefore, cold working of the exterior surface of the containment liner samples was not expected to have contributed to observed corrosion. An insignificant amount of cold working was present on the corroded side of the Liner samples. This cold working was likely the result of the water blasting that occurred during the removal of the Liner cutout from containment.
- 5.2 Technical evaluation of the corrosion product analysis and analysis of base metal corrosion front interface, as it relates to a potential corrosion mechanism in the areas of concern.
 - The original corrosion products at Area 1 and at Area 2 were removed by the water blasting. Therefore, no compound identification testing (X-ray diffraction is required) could be conducted.

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- The presence of up to 0.3% chloride on the corroded surface of one pit indicates that chloride ions may have been involved in the corrosion of the steel on the concrete side of containment samples. This concentration of chlorides is sufficient to contribute to the corrosion of steel in the presence of water and oxygen. Chlorides are catalytic in the corrosion of steel in the presence of water and oxygen. See Appendix B for a discussion of chloride effect on the oxygen concentration cell corrosion of steel.
- Sulfur was found on the corroded exterior of the steel containment liner. Since most of the sulfur was removed from the steel surface by a distilled water rinse, the sulfur compound was likely water soluble and/or water dispersible. It is known that the presence of sulfur compounds may contribute to a higher rate of corrosion of steel than would have been expected. The source of the sulfur could not be determined as the corrosion products had been removed by the water blasting.

5.3 Technical evaluation of the analysis provided by the concrete samples taken from the containment wall.

Some small voids of air were noted between the concrete and the steel containment liner sample by Beta Lab.

- In some concrete samples prepared for research studies by Florida Atlantic University, they discovered that corrosion was often found to have initiated at an air void in the steel-concrete interface. This is thought to have caused by chloride becoming concentrated at the steel-concrete interface about the void periphery and a resultant concentration or active-passive cell (or both) whereby the contiguous concrete coated and bare steel served a cathode and anode, respectively. For the high alkalinity specimens, corrosion initiation generally occurred at the larger voids. No such size dependence was disclosed for the low alkalinity specimens; however, in this case the size distribution was skewed to lower values (maximum void size 2.5 mm).⁵⁰

Water leachable and acid digested chlorides were found in the concrete samples.

- Water leachable chlorides were found at the midpoint of the concrete cover on the exterior surface of the steel containment liner. This concentration of chlorides was 0.56 PPM. The actual amount of chlorides is insufficient to be of concern as a catalyst for the corrosion of steel in the presence of water and oxygen.

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- The majority of the mill scale covered steel had no corrosion until the mill scale was removed by the water blasting.
- The pH of the concrete next to the containment liner was 10.62. Since the pH of the concrete is less than 12.5, it appears that carbonation of the concrete has occurred.
- The pH of the concrete near the midpoint of the concrete cover on the exterior surface of the steel containment liner was 10.67. Since the pH of the concrete is less than 12.5, it appears that carbonation of the concrete has occurred.
- It was observed that only very localized pitting corrosion was observed on one or two of the steel reinforcing bars removed in the containment access panel. The steel reinforcing bars had remained passive in the concrete.

Carbonation of concrete reduces the pH of the pore water in the hydrated cement paste from about 13 to a value approaching about 9. If all the calcium hydroxide is carbonated (this can take many years), the pH of the hydrated paste can reach as low as 8.3. When this happens, the durability of Portland cement is compromised in a manner described hereinafter.⁴⁴

In reinforced concrete, the steel reinforcement is surrounded by an alkaline environment (pH about or equal to 13). Under these conditions, a submicroscopic thin oxide film of ferrous oxide is formed on the steel that renders it passive, that is, it gives the steel complete protection from reaction with oxygen and water. The maintenance of the passivity of the steel is dependent on the availability of the high pH pore water solution surrounding the passive layer of ferrous oxide. When the pH of the pore water of the hydrated paste is reduced because of the carbonation, and when this low pH solution approaches the surface of the steel reinforcement, the passive oxide film is destroyed. The steel reinforcement is then open to corrosion subject to the availability of moisture and oxygen. Thus through the carbonation per se does not attack reinforcing steel, it contributes considerably to creating an environment in which corrosion of steel can take place.⁴⁴

There is a range of technical references as to when the change of pH in concrete resulting from carbonation of the concrete results in an environment being formed in which the corrosion of steel can initiate. The expert opinions vary as to the critical pH (9 to 10) below which corrosion of steel embedded in concrete may occur. These opinions include:

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- Revie, in Uhlig's Corrosion Handbook, states that steel is passivated in alkaline environments (above a pH of about 10) and assumes noble potentials. If a large passivated area in an alkaline environment is coupled to a small active area in a near-neutral environment, the latter area is attacked by the action of the passive-active cell.⁴⁴

This type of corrosion damage has frequently been observed in underground utility piping leading to steel reinforced concrete buildings. Because the steel reinforcements are in the alkaline environment of concrete (pH of about 12.5), they are in the passive state.⁴⁴

- In a 2005 paper, the authors state one of the most common forms of deterioration observed today was caused by carbonation. Carbonation is a phenomenon that occurs when carbon dioxide gas in the air penetrates concrete and reacts with hydroxides to form carbonates. The ensuing carbonation of the calcium hydroxide in the hydrated cement paste leads to the reduction in the alkalinity of the pore solution in concrete and, consequently the corrosion of the embedded steel. While carbonation does not adversely affect the concrete itself, the durability of reinforcement may be compromised because the passive ferrous oxide layer on the surface of the reinforcement breaks down when the surrounding pH falls below 9.⁴⁸

The formation of microcracks in concrete is one of the possibilities that may have occurred to the concrete pour outside the steel containment liner. In addition to normal considerations of concrete performance when in service, the concrete outside the containment steel liner is also subjected periodically to tension forces. When the steel containment liner is pressurized during testing, it may be possible that the concrete containment cover may be put into tension as the result of the slight expansion of the steel containment liner. When the internal pressure of the steel containment liner is removed after the test the steel could return to its original dimensions. However, since the concrete is not elastic, it may remain in the expanded dimension, therefore, there may be a slight separation of the steel containment liner from the concrete cover. If this very slight separation occurs, then an area where water and oxygen can collect and contribute to the formation of a potential corrosion cell may occur.

Revie states that good quality concrete that is proportioned properly, is transported and consolidated correctly, is cured adequately, incorporates supplementary cementing materials and has a low water/cement ration need not deteriorate, provided the environment for which it has been designed does not change drastically. Unfortunately, unlike steel, a factory made product, concrete is normally made at a construction site, and it does deteriorate because all the

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above requirements are not generally met. When this happens, concrete cracks giving oxygen and water access to the reinforcing steel, resulting in corrosion of the reinforcing bars and damage to the reinforced concrete structure. As cracking of concrete is very difficult to control, the only alternative then to stop deterioration of reinforced concrete is to use reinforcing bars that do not corrode. No such products are yet available on the market at a reasonable cost. It is, therefore, imperative that major research efforts be initiated to develop low-cost stainless steel reinforcement or other composite reinforcing materials that have very low tendency to corrode.⁴⁴

5.4 Water Addition to Concrete

Beside the cement and the aggregates, another potential source of chloride addition to the cement is the mixing water.

The water used in making the concrete for the containment vessel came from local wells. A water analysis was.³⁹

Chemical Analysis

pH	6.95
Alkalinity	148 mg/l
Hardness	278 mg/l
Calcium	75.2 mg/l
Calcium Carbonate	188 mg/l
Magnesium	21.9 mg/l
Sulfate	285 mg/l
Iron (total)	0.04 mg/l
Manganese	0.00 mg/l
Aluminum (+3)	0.20 mg/l
Phosphate	0.00 mg/l
Chloride	23 mg/l
Sodium	76.4 mg/l
Nitrate Nitrogen (total)	0.13 mg/l
Total Solids	480 mg/l

Based on this water analysis, the water used in mixing the original containment shell concrete is not expected to have contributed chlorides in sufficient quantity to have adversely affected the corrosion of carbon steel in contact with the concrete shell.

6.0 CONCLUSIONS AND EVALUATION

6.1 Discussion of a basis for evidence of local corrosion or general corrosion across the entire liner plate based upon the findings of 1 and 2 above.

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There is no basis for extrapolation of the corrosion observed on the removed steel Liner cutout to potential corrosion over the entire containment liner plate.

6.2 Overall assessment of identifying most likely corrosion mechanism.

The most likely corrosion mechanism of the corroded areas on the exterior steel containment liner is oxygen concentration cell corrosion. There is a possibility that chlorides may have acted as catalysts in the corrosion mechanism.

6.3 Recommended additional investigations

In order to monitor and/or control the possible corrosion on the exterior of the Containment Liner Plate a number of alternatives are suggested. Since only a small portion of the Containment Liner Plate has been inspected for corrosion, there is the possibility that corrosion may have occurred on other external areas of the Containment Liner Plate. Based on inspections of the interior surface of the Containment Liner Plate, no rust and/or blistering has been visually observed. Therefore, it can be assumed that if any corrosion has occurred on the exterior surface of the Containment Liner Plate, the corrosion has not penetrated the Containment Liner Plate. In order to monitor any possible corroding areas of the exterior surface of the containment liner, several options are given for evaluation and consideration by Beaver Valley Unit 1.

- A visual inspection of the coating applied to the interior Containment Liner should be made on a regular basis. This inspection is to detect potential blistering of the coating and rust streaking on the coating.

If blistering is discovered, the proper maintenance procedures should be implemented. These procedures should include a determination if the blistering is the result of through-wall corrosion of the Containment Liner or of another coating degradation mechanism. If through-wall corrosion has occurred then a UT evaluation of the Containment Liner for several feet around the through-wall corrosion site should be conducted. Repairs should include all additional areas where pitting may be about to occur.

If rust streaks occur on the interior surface of the Containment Liner coating, then it should be determined if the rusting is the result of a defect in the Containment Liner coating or a penetration of corrosion through the Containment Liner. The proper maintenance procedures should then be implemented. If through-wall corrosion has occurred then a UT evaluation of the Containment Liner for several feet around

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the through-wall corrosion site should be conducted. Repairs should include all additional areas where pitting may be about to occur.

- Acoustical Emission Testing may be evaluated for the entire interior surface of the Containment Liner. This testing technique may be able to detect all significant pitting that has occurred on the exterior surface of the Containment Liner.
- If water or oxygen is kept from contacting the exterior surface of the Containment Liner, then additional oxygen concentration cell corrosion of the Containment Liner cannot occur. Two techniques are suggested as possible methods for restricting water from wetting the exterior surface of the steel Containment Liner.
- It is well known that selected silicone polymers when applied to concrete can result in a significant decrease in the ability of water to penetrate concrete. Dow Corning has produced a family of water-proofing high quality silicone polymers for many years. These polymers can be sprayed on the exterior surfaces of concrete and provide many years of excellent water repellency.
- In order to determine the structural quality of the existing concrete on the outside of the steel containment liner, it is suggested that a concrete consultant be retained. He may be able through the obtaining of concrete core samples of the existing concrete containment cover at various locations, to determine the quality of the existing concrete.

7.0 POTENTIAL FUTURE CORROSION

A discussion of potential future corrosion can be found in Appendix C.

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8.0 REFERENCES

1. E. D. D. During, *Corrosion Atlas*, Case History 01.01.01.02, Third Edition, Elsevier, Amsterdam, 1997.
2. Conference Proceedings, CORROSION/96, NACE International, Houston, TX, 1996.
3. Conference Proceedings, CORROSION/97, NACE International, Houston, TX 1997.
4. Conference Proceedings, CORROSION/98, NACE International, Houston, TX 1998.
5. Conference Proceedings, CORROSION/99, NACE International, Houston, TX 1999.
6. Conference Proceedings, CORROSION/2000, NACE International, Houston, TX 2000.
7. Conference Proceedings, CORROSION/2001, NACE International, Houston, TX 2001.
8. Conference Proceedings, CORROSION/2002, NACE International, Houston, TX 2002.
9. Conference Proceedings, CORROSION/2003, NACE International, Houston, TX 2003.
10. Conference Proceedings, CORROSION/2004, NACE International, Houston, TX 2004.
11. Conference Proceedings, CORROSION/2005, NACE International, Houston, TX 2005.
12. U. R. Evans, *Mechanisms of Rusting*, pp. 813 – 831, Vol. 9, Corrosion Science, Pergamon Press, Great Britain, 1969.
13. T. Misawa, K. Hashimoto, and S. Shimodaira, *The Mechanisms of Formation of Iron Oxide and Oxyhydroxides in Aqueous Solutions at Room Temperatures*, pp. 131 to 149, Vol. 14, Corrosion Science, Pergamon Press, Great Britain, 1974.
14. Private communications with Mark Manoleras.

Draft

15. N. G. Thompson, M. Islam, D. A. Lankard, Y. P. Virmani, Environmental Factors in the Deterioration of Reinforced Concrete, p. 43-47, Materials Performance, NACE International, Houston, TX, September 1995.
16. D. W. Whitmore, *Electrochemical Chloride Extraction from Concrete Bridge Elements: Some Case Studies*, Paper No. 299, Corrosion/96, NACE International, Houston, TX, 1996.
17. *Aging Management Evaluation for Reactor Coolant System Supports*, pp. 3-14, WCAP-14422, Rev. 2, February 1997.
18. G. A. Cragnolino, D. S. Dunn, P. Angell, Y.-M. Pan, and N. Sridhar, *Factors Influencing the Performance of Carbon Steel Overpacks in the Proposed High-Level Nuclear Waste Repository*, Paper No. 147, Corrosion/98, NACE International, Houston, TX 1998.
19. *Metals Handbook*, Ninth Edition, Volume 13, Corrosion, ASM International, Metals Park, OH, 1987.
20. Steven F. Daily and Dr. Kevin Kendell, *Corrosion Protection of New Reinforced Concrete Structures in Aggressive Environments*, Paper No. 644, Corrosion/98, NACE International, Houston, TX, 1998.
21. M. Spiegel and H. J. Grabke, *Chlorine Induced Corrosion of Steels in Fossil Fuel Power Plants*, Paper No. 178, Corrosion/98, NACE International, Houston, TX, 1998.
22. Density of concrete used in exterior layer around containment steel liner.
23. Specification No. BVS-158, Revision 6, March 29, 1971, Specification for MIXING AND DELIVERING FLY ASH CONCRETE FOR BEAVER VALLEY POWER STATION – UNIT NO. 1, DUQUESNE LIGHT COMPANY.
24. G. N. Scott, *Corrosion Protection Properties of Portland Concrete*, p. 1,048 ff, Vol. 8, No. 8, Journal American Water Works Association, 1965.
25. H. H. Uhlig, *Corrosion Handbook*, p. 140, Wiley & Sons, New York, NY 1948.
26. W. F. Bogaerts, *Active Library on Corrosion 2.0*, Protective Coatings, 2.7 Mill Scale, Elsevier Science B. V., Amsterdam, The Netherlands, 1994.
27. H. H. Uhlig, *The Corrosion Handbook*, p. 388-389, John Wiley & Sons, New York, NY, 1948.

Draft

28. P. E. Zapp, *Pitting Growth Rate in Carbon Steel Exposed to Simulated Radioactive Waste*, Paper No. 129, Corrosion/96, NACE International, Houston, TX, 1996.
29. U. S. Nuclear Regulatory Commission, *Vessel Head Penetrations and Vessel Head Degradation*, 493rd meeting of Advisory Committee on Reactor Safeguards, Washington, D.C., June 20, 2002.
30. not used.
31. N. G. Thompson, M. Islam, D. A. Lankard, Y. P. Virmani, *Environmental Factors in the Deterioration of Reinforced Concrete*, p. 43-47, Material Performance, NACE International, Houston, TX, September 1995.
32. Bethlehem Steel Corporation, Report of Physical and Chemical Tests, Grade 60 Pressure Vessel (Utility Steel), Shipment 160-2963, 11/2/69.
33. Bethlehem Steel Corporation, Report of Physical and Chemical Tests, Grade 60 PVQ Steel Plates, Shipment No 409-23095, 160-3365, 11/15/69.
34. Contract Specification for Shop Fabrication and Field Erection of Reactor Containment Steel Plate Liner for Beaver Valley Power Station, Unit No. 1, Duquesne Light Company, Rev. 4, March 14, 1973, Stone & Webster.
35. Luz Marina Calle and Louis G. McDowell, *35 Years of Corrosion Protection at the Kennedy Space Center*, Paper No. 03208, Corrosion/2003, NACE International, Houston, TX, 2003.
36. R. J. Kessler, R. G. Powers, W. D. Cerlanek and A. A. Sagues, *Corrosion Inhibitors in Concrete*, Paper No. 03288, Corrosion/2003, NACE International, Houston, TX, 2003.
37. T. C. Heimel, Email "Autoscan Complete on Liner Plate", February 25, 2006.
38. Report of Tests of "Pozzolith 82" vs "Plain" concrete (A.S.T.M. Specifications C494-67T) for Master Builders Company, Cleveland, OH, Herron File D-8619, Job A-95, Herron Testing Laboratory, Cleveland, OH October 1968.
39. Bruecken Laboratory, Lab. No. 2963, May 20, 1970, Ref: Plant Well, Highway Ready Mix, Wexford, PA.
40. Telecom, F. Berry and E. Dille, March 1, 2006.
41. H. H. Uhlig, *The Corrosion Handbook*, p.126, Wiley and Sons, New York, NY. 1948.

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42. R. W. Revie, Uhlig's Corrosion Handbook, Second Edition, p. 549, Wiley and Sons, New York, NY, 2000.
43. L. L. Shreir, R. A. Jarman, and G. T. Burnstein, Corrosion, Volume 1, Metal/Environment Reactions, p.1:159, Butterworth/Heinemann, Oxford, 1998.
44. R. W. Revie, Uhlig's Corrosion Handbook, Second Edition, pp. 561-576, Wiley and Sons, New York, NY, 2000.
45. Containment Materials, Status Report, Work Tracking No. 14878, Beta Laboratory, March 3, 2006.
46. L. L. Shreir, R. A. Jarman, and G. T. Burnstein, Corrosion, Volume 1, Metal/Environment Reactions, p.3:4, Butterworth/Heinemann, Oxford, 1998.
47. G. K. Glass, A. C. Roberts, and N. Davison, Achieving High Chloride Threshold Levels on Steel in Concrete, Paper No. 4332, Corrosion/2004, NACE International, Houston, TX 2004.
48. M. A. Baccay, N. Otsuki, T. Nishida, and S. Maruyama, Influence of Cement Type and Temperature on the Rate of Corrosion of Steel in Concrete Exposed to Carbonation, Paper No. 5332, Corrosion/2005, NACE International, Houston, TX, 2005.
49. S. F. Daily and Dr. Kevin Kendell, Corrosion Protection of New Reinforced Concrete Structures in Aggressive Environments, Paper No. 644, Corrosion/1998, NACE International, Houston, TX 1998.
50. J. Nam, W. H. Hartt, and K. Kim, Time-To-Corrosion of Reinforcing Steel in Concrete Specimens as Affected by Cement Alkalinity and Bar Surface Condition, Paper No. 5256, Corrosion/2005, NACE International, Houston, TX, 2005.
51. K. Sagahara and Y. Takizawa, Development of A New Corrosion Resistant Ni-Cr-Mo-Ta Alloy with Improved Corrosion Resistance to Sulfur Dewpoint Corrosion, Paper No. 413, Corrosion/96, NACE International, Houston, TX, 1996.

APPENDIX A

FACTORS INFLUENCING CORROSION OF STEEL REINFORCED CONCRETE

Some of the documents searched for applicable references and case histories included References 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11.

Beaver Valley Unit 1 is located in a river valley where several coal-fired power plants are located nearby. The flue gases from these coal-fired power plants may be emitting a combination of gases. These gases could include: nitrogen, oxygen, water, carbon dioxide, sulfurous acid, sulfuric acid, nitrogen oxides, hydrochloric acid, unburned carbon and fly ash.⁵¹ The flue gas from the coal-fired power plants would contain a fine mist of sulfuric acid. It is possible that the sulfuric acid laden flue gas from the coal-fired power plants may be in the air surrounding the concrete shell around Containment of Beaver Valley Unit 1 when the environmental conditions make this possible. Therefore, the data provided by Evans is included for consideration in this evaluation.

Evans reported in Reference 12 that damp air, if uncontaminated, produces little or no rusting. In 1923, specimens of iron were kept over distilled water in a "desiccator-type" vessel for one month and developed only tiny dots of brown rust; even when the water contained carbon dioxide, there were only isolated rust-spots. When sulfur dioxide was present, there was rapid rusting. As pointed out by Vernon, many of the sins of sulfur dioxide have been unjustly attributed to carbon dioxide. This experiment showed that, in the absence of sulfur dioxide, as under the concrete covering of the containment vessel, a very low rate of corrosion is expected.

"When unprotected steel is submerged in oxygen containing water, a corrosion process begins that is commonly called "rusting." This rusting process is actually very complicated and is sensitive to many different parameters.¹³

"The two most important variables of iron and steel corrosion under neutral aqueous conditions are therefore (1) supply of dissolved oxygen and (2) deposited protective films. Average corrosion rates of ferrous materials submerged in quiet water containing dissolved air and free of salts that may deposit range around two to five mils per year. Conditions like agitation or mechanical aeration are accelerating, and the deposition of compounds is usually suppressing.¹²

Ferrous metals normally pit in neutral aqueous exposure because the protection afforded by rust is ordinarily irregular. Breaks in the rust layers lead to greater rates of oxygen diffusion at some points than at others. This results in oxygen concentration cells. An important fact is that rust is a conductor of sorts and may act as a cathode in the corrosion action. The features of pitting under iron rust are

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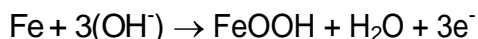
too complicated to warrant extended discussion. It is sufficient to call attention to the susceptibility of ferrous materials to pitting and to the fact that weight-loss determinations do not take pitting depth fully into account.

Passivation of Steel in Concrete

The comments regarding passivation of steel in concrete are applicable to the containment liner/concrete interface outside the containment liner.

Corrosion of steel in concrete is usually prevented by the formation on the steel of a desirable passivating gamma ferric oxide film (γ -FeOOH) that is formed in the highly alkaline environment of Portland cement concrete. Approximately 20% of hydrated Portland cement concrete is calcium hydroxide ($\text{Ca}(\text{OH})_2$) with a pH of 12.5. If sodium and potassium oxides are present in the cement, their presence typically increases the pH of concrete to values in the range of 13 to 14. Since the Portland cement concrete on the outside of Beaver Valley Nuclear Plant, Unit 1 containment liner tested to a pH of 10.6, It is expected that no sodium or potassium oxides are present in the concrete. In addition, the pH of 10.6 is an indication that carbonation of the concrete had occurred in the concrete samples.

Assuming that iron is in contact with a high pH solution, the iron will be oxidized directly to the more desirable ferric state. The half-cell reaction forming the passive film may be written as:



The same result would be expected if iron II ions were formed and immediately oxidized to iron III ions. Researchers have described a more extended process in which iron II hydroxide ($\text{Fe}(\text{OH})_2$) is initially formed and over time is oxidized to the more stable gamma ferric oxide.

Thompson¹⁵ says "that concrete is a porous solid containing an alkaline pore solution with a pH of 12.6, which promotes the formation of a passivating, protective film on the surface of the reinforcing steel. Perhaps the most important factor associated with corrosion of steel in concrete is the intrusion of chloride ions into the concrete that may break down this passive film."

"Within concrete, rebar is protected against corrosion by the alkalinity of the cement paste. Cement paste contains alkali, alkali earth, and hydroxides that give quality concrete a pH between 12 and 14 depending on source and age. In a highly alkaline environment, rebar is passivated by the formation of a surface oxide film that protects the steel from further corrosion. The oxide film is stable at pH values greater than approximately 9.5 in a chloride free environment. The pH value necessary to stabilize the passivating oxide film increases with increasing chloride content."¹⁶

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For corrosion to be initiated on the containment steel vessel and on steel reinforcing bars, it is necessary for this protective film to break down. This breakdown may occur as a result of one or both of the following causes:

- Sufficient chlorides may enter into the concrete matrix to initiate corrosion. The chlorides commonly are found in the concrete as the result of the use of de-icing salts, though exposure to a marine environment, or through the use of a concrete admixture that contains chlorides.
- Carbonation, the reaction of carbon monoxide and carbon dioxide in the air with available alkali in the concrete will gradually cause the pH of the concrete to drop over time. Once the pH is below 9.5, the passivating oxide film will start to break down.¹⁶

The main source of passivation of the steel used in fabrication of the containment liner is the passivating properties of concrete. The passivity of the steel depends upon the quality of the concrete in contact with the steel and the intimate contact of the steel by the concrete.

In conclusion, where the containment steel liner is in contact with the concrete cover, the containment steel liner at Beaver Valley Unit 1 may be passive and not subject to oxygen concentration cell corrosion. Actual inspection of the removed cutout revealed that the majority of the cutout outer surface was passive to oxygen concentration cell corrosion.

Cracking and Rebar Corrosion in Concrete

Cracking of the concrete is the path to leaking and hostile environments, which in turn become a source of further damage, such as steel rebar corrosion and concrete leaching. Under normal conditions, the highly alkaline environment of concrete provides a protective film to prevent corrosion of the steel rebar. The presence of cracks promotes the carbonation of concrete, resulting in the reduction of pH and the breaking down of the protective film, and leading to subsequent steel rebar corrosion. The rust expands and creates tensile stresses on the concrete, thus causing spalling and more cracking. In addition to a path for the ingress of carbon dioxide into the concrete, the cracks also provide a path for water, oxygen, and chlorides to penetrate into the concrete.

Since the containment vessel is pressurized in order to perform required containment integrity tests periodically, the concrete on the outside of containment is put into tension. As a result of this condition of being in tension, it is possible that fine hairline cracks may develop in the concrete. If the hairline cracks formed, their presence would provide a mechanical path for moisture to move through the concrete and to contact the outside of the steel containment liner.

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Only two small areas of pitting corrosion were observed on the steel reinforcing bars that were removed from the concrete over the water blasted concrete. Since the reinforcing steel (rebar) had very minimal localized rusting, the main path of the oxygen to the outside of the containment steel liner is likely from another source or location in the concrete structure. This alternative source or location of the oxygen to support the observed oxygen concentration cell corrosion in the pitted areas was not found.

Aggressive Environments

Leaching and aggressive chemicals can cause the deterioration of concrete. Leaching is a phenomenon that occurs at those parts of concrete where water enters and passes through a concrete body, washing out the readily soluble calcium hydroxide and other solids. As a result, the porosity of the concrete is increased, boosting vulnerability to a hostile environment while reducing strength. The rate of leaching decreases as the amount of dissolved salts contained in the percolating water increases. The rate is higher in cold water due to higher solubility of calcium hydroxide at lower temperatures. Note that leaching is significant only when water flows into cracks or improperly constructed joints. Leaching also results from alternating and successive wetting and drying of concrete. Groundwater that is flowing on a concrete surface is not expected to cause leaching. The product of leaching, when dried and deposited on a concrete surface, is known as efflorescence. The presence of efflorescence is an indication of leaching. No efflorescence was seen on the outside of the containment concrete.

Because of the alkalinity of hydrated cement paste, acidic material can attack concrete readily. However, note that a minimum concentration must be maintained to have a significant chemical attack. Sulfates of sodium, potassium or magnesium are harmful chemicals that can attack the hydrated lime and hydrated calcium aluminate in cement paste. The calcium sulfate dihydrate and calcium sulfoaluminate formation is associated with considerable expansion, which disrupts the concrete. Sodium sulfate can form Glubber's Salt and result in expansion of the concrete with resulting cracks when the sodium sulfate crystallizes.

Based on the Nuclear Management and Resources Council (NUMARC) Class I structures industry report,¹⁷

- Concrete exposed for extended periods to aggressive chemicals (<5.5 pH) or chloride or sulfate solutions beyond defined limits (500 ppm chlorides, and 1,500 ppm sulfates) can undergo significant chemical attack.
- Concrete exposed to the above environment for intermittent periods only will not have significant degradation.

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For the potential of corrosion to be significant, concrete must be exposed to the corrosive environment for extended periods of time. Cracks must occur to allow aggressive chemicals to reach the reinforcement.

Elevated Temperature

The production and handling of steam and the nuclear fission process generate large thermal loads on nuclear plant components. Sustained exposure to high temperatures (300°F or higher) or to numerous hot-cold cycles may cause the concrete to deteriorate, with surface scaling and cracking becoming visible. The key locations include hot process and steam piping penetrations, reactor biological shield, steam-driven equipment pedestals, locations in the turbine building, and certain equipment supports.

Concrete temperature at operating conditions should not exceed 150°F, and local area temperatures should be kept below 200°F. The maximum average operating temperature at Beaver Valley Nuclear Plant, Unit 1, is about ambient; thus, the concrete at its interface with the containment vessel is not subjected to elevated expenses at normal operating conditions.

Radioactivity

Many studies on the effects of radiation on concrete properties have been conducted. It has generally been concluded that damage to the concrete by radioactivity is far less than that by temperature effects. At Beaver Valley Unit 1, the amount of radiation to which the concrete liner would be exposed is considered minimal.

Relative Humidity

“Atmospheric corrosion takes place only when the metal surface is covered by a water film of sufficient thickness to sustain electrochemical reactions. Water can be physically adsorbed to the metal surface in molecular form or it can be chemically bonded in a dissociated form that results in the formation of metal-hydroxide bonds. Both molecular and dissociative bonding occurs on metal oxides. The metal-hydroxyl film is actually quite protective and can be formed at low values of relative humidity (approximately 20 percent). At approximately 40 percent relative humidity, an additional highly immobile water layer is adsorbed onto the metal-hydroxyl film. The critical relative humidity above which atmospheric corrosion of most metals occurs corresponds to the relative humidity necessary for the formation of a liquid film composed of multiple water monolayers that displays properties similar to those of bulk water.”¹⁸

“Iron and steel exhibit a primary critical relative humidity around 60 percent, similar to most metals. Below 60 percent relative humidity, corrosion proceeds at a slow rate, but at 75 to 80 percent relative humidity, the corrosion rate sharply

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increases. This secondary critical relative humidity is attributed to capillary condensation of water in the pores of the solid corrosion products. The water films that form on the metal surface usually contain a variety of contaminants, including trace amounts of chlorides and other soluble species such as carbon dioxide that increases the electrical conductivity and decrease the pH of the film, leading to an increase in the dissolution of the iron or steel.”¹⁸

Studies have shown that the duration of wetness, although an important factor, cannot be considered in isolation when estimating corrosion rates. An excellent example of this fact is demonstrated in Figure 1, in which the weight gain of iron is plotted as a function of the relative humidity for 55 days of exposure in an atmosphere containing 0.01% sulfur dioxide. In the lower right hand corner of Figure 1 is the major corrosion rate for iron exposed for the same time in a sulfur-dioxide-free atmosphere at 99% relative humidity. The increase in the corrosion rate produced by the addition of sulfur dioxide to the atmosphere is substantial. In addition, the figure above shows a critical value near 60% relative humidity.¹⁹

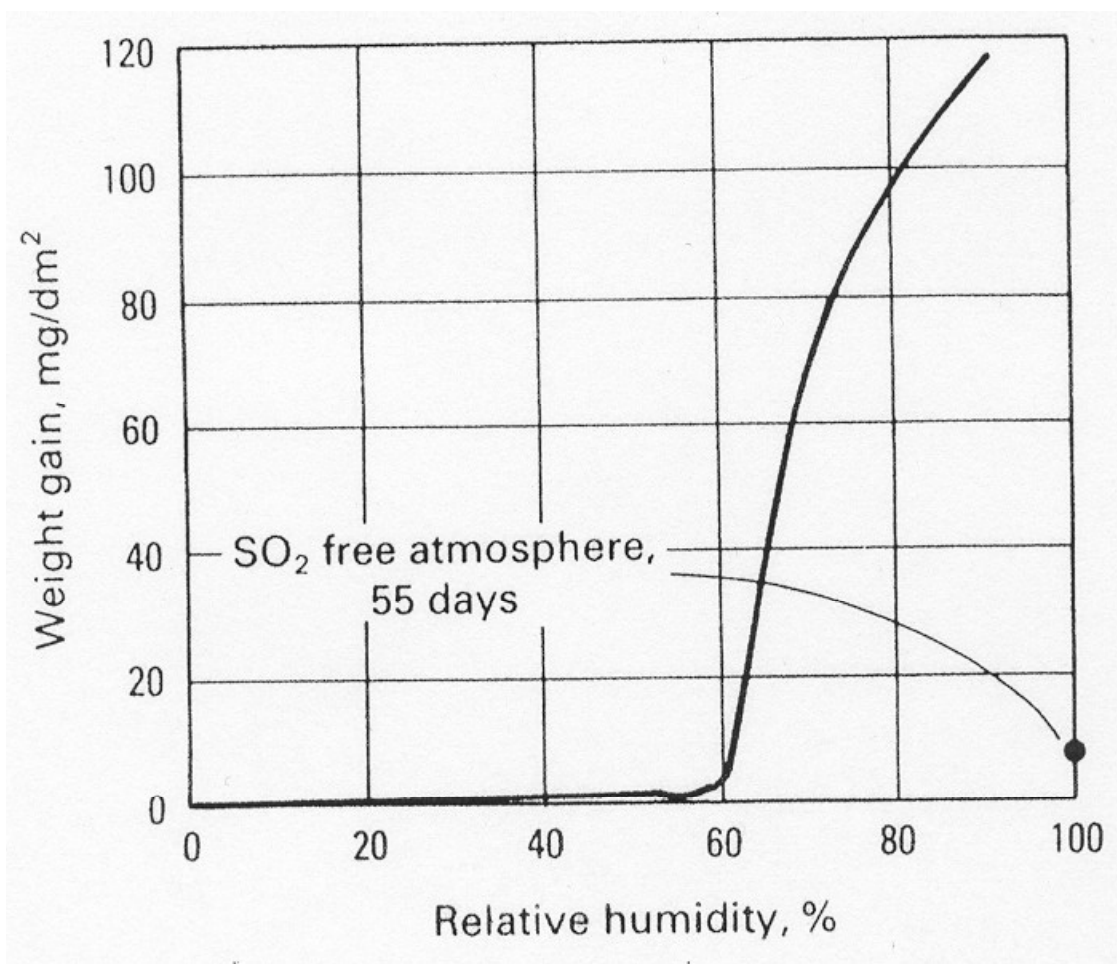


Figure 1. Effect of Relative Humidity and Atmospheric Pollution on the Rusting of Iron

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Cold-Wall Effect

One of the potential corrosion mechanisms that may occur when the corrosion of steel is being evaluated is the cold-wall effect. When the temperature of the steel being subjected to potential corrosion is below the dew point of the air in which the steel is exposed, then condensation of water may occur on the steel. This condensate will be distilled water. Since distilled water contains no dissolved ions and/or compounds and desires to be saturated with ions, a driving force is created in the condensate. This driving force results in ions and oxygen being drawn to the condensate. The resultant mixture of ions and oxygen on the steel results in the formation of a potential corrosive environment and corrosion of the steel. The cold-wall effect is a significant potential corrosion mechanism for coatings applied to steel.

The cold-wall effect is not considered a significant corrosion consideration at Beaver Valley, Unit 1 for the corrosion of the exterior of the concrete covered containment liner.

Carbon Dioxide

Although chloride is the main source for corrosion of reinforcing steel, concrete carbonation leads to a uniform corrosion of steel that accelerates the crack formation and decreases the reinforced steel concrete service life. Improving the concrete quality and cover thickness generally minimizes this carbonation-induced corrosion.

Carbonation of concrete is well known in marine environments. Acidification of concrete due to carbon dioxide can occur in places where the right climate conditions are available for uniform corrosion to develop. This uniform carbonation-induced corrosion accelerates the concrete crack formation and decreases the residual service life of the concrete structures.

Chlorides

“Chloride ions do not take part in the corrosion process *of steel* since they act only as catalysts. The corrosion reaction rate is therefore controlled by the supply of cathode reactants, such as water and oxygen, to the cathode side of the corrosion cell. These species are consumed at the cathode and consequently the greater their supply, the greater is the corresponding loss of metal at the anode. For these reasons, structures which are partially exposed to the atmosphere and partially submerged in the chloride-contaminated waters are at greater risk to corrosion, since they contain all the requirements for corrosion at a single site.”²⁰

Since chlorides are a significant material for the potential corrosion of steel in concrete, it is important to determine the leachable chlorides in the materials that

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will be in contact with the steel. Therefore, each of the materials recommended to be used in this report was evaluated for potential leachable chlorides.

“Since oxygen depolarization controls the rate throughout the sodium chloride concentration range, it is (of) some interest to understand why the rate first increases, reaching a maximum of about 3 percent sodium chloride and then decreases. Oxygen solubility in water decreases continuously with sodium chloride concentration, explaining the fall off of corrosion rate at the higher sodium chloride concentrations. The initial rise appears to be related to a change in the protective nature of the diffusion barrier rust film that forms on corroding iron. In distilled water having low conductivity, anodes and cathodes are always in the proximity of iron II ions forming at near by anodes, resulting in a film of iron II hydroxide adjacent to and adherent to the metal surface. This provides an effective diffusion barrier film.”²¹

In sodium chloride solutions, on the other hand, conductivity is greater; hence, additional anodes and cathodes can operate much farther removed one from the other. At such cathodes, sodium hydroxide does not react immediately with iron II chloride, formed at anodes; instead, these substances diffuse into the solution and react to form iron II hydroxide away from the parent metal surface. Any iron II hydroxide so formed does not provide a protective barrier layer on the metal surface. Hence, iron corrodes more rapidly in dilute sodium chloride because more dissolved oxygen can reach cathodic areas. Above 3% sodium chloride, the continuing decreased solubility of oxygen becomes more important than any change in the diffusion barrier layer, hence corrosion decreases.”²¹

Thompson performed extensive controlled experiments for six months to determine the corrosion of standard reinforcing steel embedded in mortar. A full matrix of experiments was performed for three chloride levels, three temperatures, and three humidities. These data along with the test conditions are summarized later in this report in Table 12¹⁵

“The mechanism of the chloride corrosion is explained as follows. In conventional concrete, chloride ions may be present in the aggregate or mix water or may be introduced as calcium chloride used as a curing accelerator (admixture), through the migration of deicing salts, seawater, or air borne salts in marine environments or from other sources. Once the chloride ion concentration reaches a critical concentration, chloride-related corrosion sets in and corrosion products build up. The iron corrosion products occupy 7 to 10 times more volume than the original steel. Lack of concrete capability to bear these expansive forces results in concrete cracking.”¹⁵

It is significant to note that no significant cracking of the concrete around the steel containment vessel was observed. There are no visible chloride-related corrosion effects at any elevation observed from the ground surrounding the concrete dome.

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Because of dominant role of chloride ions in the corrosion process of steel embedded in concrete, the vast majority of research on protection of concrete focuses on changes to the concrete that can reduce the rate of chloride ion diffusion. Once chloride ions reach the level of reinforcing steel and moist concrete, corrosion will occur when a critical range of chloride concentration is reached, if oxygen is available.

Factors that have been shown to affect the corrosion of embedded reinforcing steel in concrete, once chloride ions reach the steel, include the following:

- The number of chloride ions present in the areas adjacent to the concrete.
- Temperature
- Relative Humidity

The absence of chloride ions adjacent to the concrete is exemplified by the lack of chloride ions found in the external pitted steel.

The chloride concentrations in the tables by Dr. Thompson are converted to ppm by this sample calculation and presented in Table 12. For the calculation, the density of concrete used in containment is about 147 lb/cu. ft.²² (The average density of the Pozzolite 82 concrete used at Beaver Valley was about 147.9 lb/cu. ft.)³⁸

$$(1 \text{ lb chlorides/cu yd concrete})(1 \text{ cu yd}/27 \text{ cu ft})(\text{cu ft}/147 \text{ lb concrete})(\text{ ppm}) = 252 \text{ ppm chlorides}$$

In conclusion, for corrosion of steel in contact with concrete to occur at a measurable rate, the chloride concentration must exceed 252 ppm. The field investigation results indicate a water leachable chloride concentration at the Beaver Valley Unit 1 external containment concrete of less than 0.56 ppm.

Concrete Mix

Measurements of the type and amount of chemical species in concrete pore solutions are quite routine functions. Particular interest is focused on measurements of the chloride/pH effect. It is now well established that the depassivation of embedded steel, where it occurs, is a function not only of chloride ion concentration, but also of hydroxide ion concentration. The specification for the concrete²³ used in the Beaver Valley Unit 1 containment cover did not allow the addition of chlorides; thus, the chloride/pH effect would be low.

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Fly Ash Addition to Concrete

It was stated that the concrete outside of containment liner contains fly ash. This fly ash was alleged to have come from local power plants belonging to Duquesne Light.¹⁴

Studies were conducted by the Florida Department of Transportation in cooperation with the University of South Florida to compare the behavior of various corrosion inhibitors for steel in concrete. Three commercially available inhibitors (two based on organic compounds and one calcium nitrite-based) were selected for the study. Each inhibitor was evaluated in several types of concrete mix designs. The mixes included Portland cement concrete as the control, concrete admixed with silica fume, and concrete admixed with fly ash for comparison. Standard specimens containing either of the two organic corrosion inhibitors performed relatively equal to control specimens (Type II cement, no pozzolans, no inhibitors). Standard specimens containing silica fume exhibit no corrosion activity. The present data indicated that calcium nitrite-based inhibitor was effective in mitigating corrosion in high permeability concretes. However, low-permeability concrete specimens containing pozzolans (particularly silica fume) continue to exhibit a significantly longer time to corrosion initiation than specimens containing only conventional inhibitors. In fly-ash admixed concrete (no inhibitor added) there was at least a three-fold increase in Time to Corrosion Initiation (TCI) and Time to Failure (TTF) over that of the non-fly-ash control mix.³⁶

The fly ash that was added to the containment concrete is expected to increase the amount of time before the exterior surface of the containment steel liner would initiate rusting over that which would have occurred if a standard concrete had been used.

Oxygen Availability

Scott noted that dissolved oxygen, being limited to a few parts per million, normally does not initiate corrosion in submerged concrete because not enough oxygen is available for the cathodic reaction.²⁴

It was observed on the steel plate that had been cut from the containment liner that the original mill scale was adhered to most of the exterior/concrete side of the steel plate. The presence of the mill scale indicates that there was insufficient amount of oxygen and/or water to have initiated corrosion over most of the steel plate.

In conclusion, the concrete surrounding the containment vessel is expected to have minimal oxygen availability to conceivably produce any significant corrosion on the steel liner.

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Steel Liner Plate Characteristics

One of the parameters that affects the corrosion of metals is the composition of the metal exposed to the corrosive environment. Therefore, it is important to know the composition of the steel that is in the corrosion system being studied.

The containment steel liner was fabricated of steel that was made per ASTM A 516, Grade 60, fine grained, normalized, minimum, NDT –20 F, Pressure Quality.³⁴ The composition of the steel is given as follows:

Table 1. Composition of Steel

Analysis of Steel Plates Installed at the Locations of Observed Corrosion

The majority of the steel plate on which the corrosion was observed was fabricated of Mill Order No. Z77645 (Heat No. 485Z0981).

Section Slab Mill Order No.	Heat No.	Description	Thickness	Yield Point	Tensile Strength	Elong %	C	Mn	P	S	Si
Z77645	485Z0981	1-412 x 126	3/8	48500	69700	26.0	.18	.72	.009	.023	.23
Z76332	485Z1291	1-412 x 126	3/8	48200	68900	27.0	.17	.71	.010	.029	.23

Plates and Test Pieces Normalized at 1650 Deg. F.

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Because carbon steels are by definition not very highly alloyed, it is not surprising that most grades do not exhibit large differences in atmospheric corrosion rate. Nevertheless, alloying can make changes in the atmospheric corrosion rate of carbon steel. The elements generally found to be most beneficial in this regard are copper, nickel, silicon, chromium, and phosphorus. Of these, the most striking example is that of copper; increases from 0.01% to 0.05% have been shown to decrease the corrosion rate by a factor of two to three. Combinations of the above elements are generally more effective at reducing the corrosion rate than the elements individually, although the effects of the combinations are not the sums of the individual effects. The effectiveness of these elements in retarding corrosion also appears to depend on the corrosive environment, with the most benefit appearing in industrial atmospheres.

The effect of each of the elements found in ASTM A 516 steel used for the fabrication of the containment steel liner on the projected corrosion is discussed below:

- **Carbon.** In fresh waters, the carbon content of iron is not of practical importance in determining the corrosion rate. In sea water, there is a slight increase in the corrosion rate with higher carbon steels, but again this is not of great significance.²⁵

In acids, the effect of carbon is complicated by the factor of heat treatment and by the appreciable effect of minor elements often present, such as copper. In general, the corrosion rate increases with increasing carbon content. High-carbon steels, however, are more readily passivated by nitric acid than are low-carbon steels. High carbon was also found beneficial in steels used to resist mixtures of sulfuric and nitric acid.²⁵

Increasing the carbon content of a steel from 0.09% to 0.28% increased the resistance to intergranular stress corrosion cracking.²⁵

- **Manganese, Sulfur, Phosphorus, Silicon.** These elements of ordinary constructional steels, present in usual amounts, have no effect of any commercial significance on corrosion in fresh or salt waters. In acids, silicon in normally small percentages has no appreciable effect on the corrosion rate of iron. The 14% to 15% Si-Fe alloy, however, is acid resistant.²⁵

The presence of manganese, sulfur, and phosphorus in steels tends to increase corrosion in acids. Manganese has less effect in this respect than sulfur or phosphorus.²⁵

In conclusion, it is considered that the amounts of the elements present in the carbon steel used for fabrication of the containment liner reflects the normal distribution for steel. No adverse effect on this steel is expected.

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Mill Scale Effect

Since the exterior surface of the steel used in the fabrication of the containment liner was covered with mill scale and this mill scale was not removed before the exterior concrete was installed, a discussion of mill scale effects on corrosion is presented.

Mill scale, or blue scale as it is sometimes called, forms on steel as it is hot rolled, and varies according to the type of operation and rolling temperature. It is not a complex subject, but since the majority of structural steel is hot rolled, the quantity of surface contaminated with mill scale is important.

“In general, mill scale is magnetic and contains three layers of iron oxide, although the boundaries between the oxides are not particularly sharp. The thin outer layer of mill scale is essentially iron II oxide, which is relatively stable and does not easily react. The layer closest to the steel surface, and sometimes intermingled with the steel’s surface crystalline structure, is iron II oxide. This is an unstable substance that is easily oxidized to iron III, resulting in a chemical change to iron III oxide. This process, accompanied by an increase in volume, results in loosening the intact mill scale, particularly during weathering or where moisture is present.”²⁶

In the field of corrosion, many studies are conducted in seawater as the tests can then be compared in many parts of the world. There is variation in the corrosivity of seawater depending on where the seawater is located but there are comparative corrosion studies also available to correlate seawater corrosivity. Thus, in this work referenced by Uhlig, all of the corrosion studies on carbon steel were conducted in seawater. The corrosion rates obtained from sea water tests would be expected to be higher than those obtained if fresh water had been used for the same tests.

The depth of pitting in carbon steel is influenced considerably, especially during the early stages of exposure in seawater, by the presence of mill scale. So long as mill scale remains in place, it acts to accelerate corrosion at bare spots or breaks in the scale through the action of galvanic cells set up between the scale-covered steel and the bare steel. The extent of this acceleration is determined roughly by the relative areas of bare steel and scale-covered steel, since the effect is to concentrate all corrosion on the bare spots with consequent increase in the depth of attack in such areas. The extent of the acceleration of corrosion by mill scale and the relative area effected are shown by the data in Table 10 obtained by immersion of scaled steel specimens in seawater from which definite areas of the scale had been removed before exposure.²⁷

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Table 2. Relationship Between Area of Bare Metal and Depth
Of Attack of Partially Descaled Steel²⁷
(Specimens immersed in salt water for 4 months at Fore River, MS)

Bare Area as Percentage of Total	Ratio of Sealed to Bare Area	Observed Depth of Attack In Bare Area, mpy
5	19:1	45
10	9:1	35
25	3:1	15

It may be stated as a general rule that steel exposed in seawater with mill scale present will be pitted about three times as deeply as descaled steel for short period of exposure, such as a few months. This ratio decreases as the exposure is prolonged and is about 1.5 to 1.0 for a 10-year exposure period. It follows, then, that the desirability of removing mill scale before exposure is greatest when the thickness of the steel is small and when pitting would result in failure of the metal to accomplish its purpose. Removal is less important when the sections are relatively large, for pitting is then less important and the period of exposure is likely to be long as with steel piling.²⁷

The pitting factor varies between scaled and descaled steel. It also varies with the incidental conditions and with the duration of exposure, that is, the longer the exposure, the lower the pitting factor. A normal pitting factor for exposures of about 10 years would be about 2.5 for descaled steel, and 3.5 for steel exposed with mill scale. Applying these factors to the normal corrosion rate as indicated by weight loss, the deepest attack on descaled steel would be about 15 mpy and would be 20 mpy on steel exposed with mill scale over a 10-year period in seawater.²⁷

However, for short periods of exposure in seawater, e.g., less than a year, the rate of pitting might be as much as 40 mpy for descaled steel, and 100 mpy for steel exposed with mill scale. In view of the variability of the several factors that influence pitting, these suggestions of what may be considered normal rates should be used primarily as a basis for deciding whether there may be correctable causes for much higher observed rates of pitting, rather than for estimating probable life of steel under conditions of exposure that have not been investigated. However, they are probably better than a guess for the latter purpose.²⁷

Potential Corrosion Rates of Mill Scale Coated Carbon Steel

The measured corrosion rate of the corroded carbon steel on the exterior of the containment liner (under the structural fly-ash concrete) can be compared to the known corrosion rate of carbon steel at a variety of standard test locations. A comparison of 11 test locations are shown in Table 3. The Pittsburgh, PA location had a corrosion rate of 1.2 mpy. This would be the expected corrosion

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rate of mill-scale covered carbon steel exposed to the natural elements at the Beaver Valley Nuclear Plant, Unit 1.

Table 3. Comparison of Corrosion Rates of Carbon Steels at Various Test Locations³⁵

Location	Type of Environment	$\mu\text{m/yr}$	Corrosion Rate (a) Mils/yr
Esquimalt, Vancouver Island, BC, Canada	Rural marine	13	0.5
Pittsburgh, PA	Industrial	30	1.2
Cleveland, OH	Industrial	38	1.5
Limon Bay, Panama, CZ	Tropical marine	61	2.4
East Chicago, IL	Industrial	84	3.3
Brazos River, TX	Industrial marine	94	3.7
Daytona Beach, FL	Marine	295	11.6
Pont Reyes, CA	Marine	500	19.7
Kure Beach, NC (80 ft. From ocean)	Marine	533	21
Galeta Point Beach, Panama CZ	Marine	686	27
Kennedy Space Center, FL (beach)	Marine	1070	42

(a) Two-year average

The principle mechanism of deterioration of concrete structures in aggressive environments is created by chloride contamination of the concrete. These ions migrate through the concrete mix until they reach the surface of the steel reinforcement. The rate at which this occurs is dependent on several factors including the concrete cover, concrete permeability, drainage, wetting and drying cycles, temperature, degree of cracking and the effectiveness of other protection methods. Chlorides can also be introduced into the concrete by the use of contaminated aggregates, deliberate addition of chlorides as set accelerators, and the use of seawater in the mix or for curing. In aggressive environments, it is not unusual for chloride ion levels to exceed 0.3 percent by weight of concrete at a depth of 75 mm (3 in.) below the concrete surface after only 10 years of service. In such cases, visible signs of deterioration have been reported to develop in less than seven years.⁴⁹

Since Beaver Valley Unit 1 is located near several coal-fired power plants, it is possible that the exhaust gases from these power plants may have deposited corrosive compounds from the flue gas onto the outer surface of the concrete cover of containment.

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The levels of chloride required to initiate corrosion are extremely low. There have been many recommendations, both codes and publications, for maximum chloride concentrations. The American Concrete Institute (ACI) Committee 222, recommends the following chloride limits in concrete for new construction, expressed as a percent of weight of cement (acid-soluble test method).

- Pre-stressed concrete 0.08 percent
- Reinforced concrete in wet conditions 0.10 percent
- Reinforced concrete in dry conditions 0.20 percent

A chloride threshold for corrosion also exists in terms of the chloride/hydroxyl ratio. It has been reported that when the chloride concentration exceeds 0.6 of the hydroxyl concentration, corrosion is observed. This approximates to a concentration of 0.4% chloride by weight of cement if chlorides are cast into the concrete and 0.2% if they diffused into the hardened matrix.⁴⁹

Chloride ions do not take part in the corrosion process since they act only as catalysts. The corrosion reaction rate is therefore controlled by the supply of cathode reactants, such as water and oxygen, to the cathode side of the corrosion cell. These species are consumed at the cathode and consequently the greater their supply, the greater is the corresponding loss of metal at the anode. For these reasons, structures which are partially exposed to the atmosphere and partially submerged in chloride contaminated waters are at greatest risk to corrosion since they contain all the requirements for corrosion at a single site.⁴⁹

APPENDIX B

PROBABLE CAUSE OF CONTAINMENT LINER CORROSION

Pitting Corrosion of Steel

“The definition of pitting rests upon the concept of passivity in metals. Pitting is the local electrochemical dissolution of metal from a surface that is electrochemically passive. Passivity arises from the growth of a stable, non-porous oxide film that markedly impedes the rate of general dissolution of the alloy in reactive environments. Pitting is inherent in the performance of engineering alloys, such as iron- and aluminum-based alloys, because these alloys derive their utility and stability in potentially corrosive environments from the presence of a passive oxide film on their exposed surfaces. Pitting may begin with a small, randomly located breach of the passive film, which exposes the underlying alloy to the environment and active corrosion. The anodic reactions in the initiated pit can occur at a very high rate because the supporting cathodic reactions take place on the large remaining passive surface. Most of the surface undergoing pitting continues to be passive. The ratio of pitting current density to passive surface current density may be as high as 10.²⁸

“Pitting is perhaps the most difficult corrosion form to evaluate and characterize in an engineering structure or component, because of the randomness of its initiation and propagation. Ives has defined five stages in the development of a corrosion pit: (1) local breakdown of the passive film, (2) high anodic dissolution current density, (3) competition between repassivation and establishment of continuing pit growth, (4) growth from atomic scale to microscopic scale, and (5) growth from microscopic to macroscopic size, or simply, macroscopic pitting. The literature on pitting is extensive and largely focused on its early stages. From the point of view of engineering service of materials, macroscopic pitting is of greatest interest. It is typically the through-thickness macroscopic pit that results in the failure of a structure. However, stage (5) pit growth is far less studied than the earlier stages. This is probably due to the random nature of the growth, growth rate, and cessation of growth and the cost and technical challenges in the study of macroscopic pitting. The successful approach to understanding macroscopic pit growth is based statistically on measurements of large populations of pits.²⁸

Corrosion Caused by Differential Aeration (now called Oxygen Concentration Cell)

Oxygen as described previously is a chief factor in the general corrosion of iron immersed in water, but in addition it can cause localization of attack through so-called differential aeration cells (now called oxygen concentration cells). These cells are formed whenever iron is in contact with aerated solution at one place and

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with oxygen-deficient solution elsewhere. The oxygen-deficient areas become anodes and therefore suffer proportionately more corrosion. Differential aeration cells commonly account for localized corrosion or pitting under partially protective rust layers on iron, in open crevices, or whenever aerated solution is shielded from portions of an iron surface.⁴¹

In a discussion of the corrosion of steel in seawater an excellent comment about how mill scale affects the observed corrosion is presented. This discussion related to Beaver Valley as chlorides are involved in the corrosion of the steel containment liner at Beaver Valley.

One of the common causes of pitting of carbon steel is differential aeration cells formed by nonuniformity of corrosion product films or spotty coverage of fouling organisms on the surface. Mill scale, if it has not been removed prior to exposure to seawater, accelerates corrosion at bare spots or breaks in the scale through galvanic action, resulting in pits. Galvanic action tends to decrease with time because the mill scale is undermined by corrosion products that cause it to be spalled off. For this reason, the effect of mill scale is more pronounced during the early stages of exposure.⁴²

From Reference 43, there is a discussion of differential aeration localized corrosion (oxygen concentration cell corrosion):

Before considering the factors that complicate localized attack it is relevant to refer to some of the classical work of U. R. Evans on differential aeration. Perhaps the simplest example, although in corrosion science nothing is as simple as it first appears, is the distribution of anodic and cathodic sites produced when a drop of an electrolyte solution (e.g. sodium chloride or sodium sulfate) is placed on a horizontal steel surface. Assuming that no dissolved oxygen is present initially and that mass transfer occurs solely by diffusion, it is apparent that transport of oxygen from the atmosphere to the surface of the metal by diffusion will occur most rapidly through the thin layer of solution at the periphery of the drop and most slowly at the center of the drop. Thus the metal surface adjacent to the periphery will become the cathode of the differential aeration cell while the metal in the interior will become the anode. (see Figure 2). The hydroxyl (OH^{-1}) ions formed by the cathodic reduction of dissolved oxygen and the ferrous (Fe^{+2}) ions formed by anodic dissolution will be brought together by migration and diffusion and will combine to form ferrous hydroxide ($\text{Fe}(\text{OH})_2$) that is rapidly oxidized by the dissolved oxygen to rust ($\text{Fe}_2\text{O}_3 \bullet \text{H}_2\text{O}$).⁴³

PRINCIPLES OF REINFORCEMENT CORROSION IN CONCRETE⁴⁴

As concrete is porous and both moisture and oxygen can move through the pores and microcracks in concrete, the basic requirements for corrosion of mild or high strength ferritic reinforcing steels are present. The reason that corrosion does not occur in most cases is that the pores contain high levels of calcium, sodium, and potassium hydroxide, which maintain a pH of between 12 and 13. This high level of alkalinity passivates the steel, forming a dense gamma ferric oxide that is self-maintaining and prevents rapid corrosion.

In many cases, any attack on reinforced concrete will be on the concrete, However, there are two chemicals that penetrate the concrete and attack the steel without breaking down the concrete first. The culprits are chlorides and carbon dioxide as these are the main common atmospherically borne species that penetrate concrete without causing significant damage and then promote the corrosion of steel by removing the protective passive oxide layer on the steel, created and sustained by the alkalinity of the concrete pore water.

Figure 1 shows the electrochemical corrosion mechanism common to both carbonation and chloride-induced corrosion. The separation of anodes and cathodes is an important part of the understanding, measurement, and control of corrosion of steel in concrete. Corrosion of steel in concrete is basically an aqueous corrosion mechanism where there is very poor transport of corrosion product away from the anodic site. This usually leads to the formation of voluminous corrosion product and cracking and spalling of concrete, with delaminations forming along the plane of the reinforcing steel. In the absence of sufficient oxygen at the anodic site, the ferrous ion will stay in solution or diffuse away and deposit elsewhere in pores and microcracks in the concrete, leading to severe section loss without the advanced warning given by concrete cracking and spalling.

CHLORIDE INGRESS AND THE CORROSION THRESHOLD⁴⁴

Chlorides can be present in concrete for a number of reasons:

1. Contamination
 - a. Deliberate addition of calcium chloride set accelerators.
 - b. Deliberate use of sea water in the mix.
 - c. Accidental use of inadequately washed marine sourced aggregates.
 - d. Other sources.
2. Ingress
 - a. Deicing salt ingress.
 - b. Sea salt ingress.
 - c. Chlorides from chemical processing, and so on.

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Until the later 1970's, it was widely held that chlorides cast into concrete were largely bound as chloroaluminates and would not cause corrosion. It was then found that large numbers of structures with chloride cast into the mix did suffer from corrosion and that binding was not as effective as initially believed. The ACI Report 222R-96 reviews the national standards and laboratory data. The consensus is that a chloride level of 0.4% chloride by weight of cement is a necessary but not sufficient condition for corrosion and that in variable chloride and aggressive conditions corrosion can occur at lower chloride levels, down to about 0.2% chloride by weight of cement.

A recent literature review suggested that whether chlorides are bound or not, the chloroaluminates break down releasing chloride ions for participation in the passivation breakdown process. They suggested that the discussion about the amount of chloride bound in the cement paste is therefore less important than previously thought. They also pointed out that the amount of calcium hydroxide available to maintain the pH has a profound effect on initiation of corrosion. This has implications for cement replacement materials.

CARBONATION OF CONCRETE AND THE CONSEQUENCES OF CORROSION⁴⁴

Carbonation is a simpler process than chloride attack. Atmospheric carbon dioxide reacts with the pore water to form carbonic acid. This reacts with the calcium (and other) hydroxides to form solid carbonates. The pH therefore drops from about pH 12 to about pH 8. The steel starts to corrode at around pH 11.

Carbonation is associated with poor concrete cover, poor concrete quality, poor consolidation, and old age in the absence of chlorides. Carbonated concrete is good quality concrete but it is no longer protective to the reinforcing steel.

Carbonation rates are a function of the environment where indoor concrete will carbonate faster than outdoor concrete in North America and Northern European environment, but wet/dry cycling in warm conditions can accelerate carbonation in more southern latitudes. As corrosion will not proceed in the absence of water, carbonation rates are usually unimportant inside buildings except in bathrooms, kitchens, and other situations where there is wet/dry cycling and sufficient moisture to cause carbonation to rebar depths.

METHODS FOR DETECTING AND MEASURING CHLORIDE IN CONCRETE⁴⁴

Chloride Content.

Chlorides can be cast into concrete or can be transported in from the environment. The chloride ion attacks the passive layer even though there is no significant drop in pH. Chlorides act as catalysts to corrosion. They are not consumed in the

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process, but help to break down the passive layer of oxide on the steel and allow the corrosion process to proceed quickly. Chloride contents are measured by sampling the concrete and analyzing a liquid extracted from the sample. This is usually done by mixing acid with concrete dust from drillings or crushed core samples. An alternative is pore water extraction by squeezing samples of concrete or, more usually, mortar. The pore squeezing technique is frequently used in laboratory equipment work as it is often difficult to extract useful pore water samples from field concrete. A third technique is to crush concrete and boil it in water to extract water-soluble chlorides only.

As well as acid soluble chloride, there are the water soluble chloride tests (ASTM C 1218, American Association of State Highway Officers (AASHTO) Test T 260 and Federal Highway Administration Report FHWA RD-77-85). These techniques use different levels of pulverization of large samples that are refluxed with water to extract the supposedly unbound chlorides. These chlorides are, or can become, free in the pore water to cause corrosion as opposed to chlorides bound by the aluminates in the concrete, or bound up in some aggregates of marine origin. The water soluble chloride test is rather less accurate than the acid soluble test because some of the “bound” chlorides can be released, and the finer the grinding the more will be extracted. However, this test can be useful in showing the corrosion condition where chlorides have been cast into concrete, and particularly where aggregates are known to contain chlorides that do not leach into the pore waters.

The corrosion threshold is usually given as about 0.4% chloride by weight of cement, 0.05% chloride by weight of concrete, or 1.2 lb/cu.yd. of concrete. This is only an approximation because:

- a. Concrete pH (about $14 - \log_{10}$ of the hydroxide concentration), varies with the cement powder and the concrete mix. A small pH change is a massive change in hydroxide concentration, and therefore the threshold moves radically with pH.
- b. Chlorides can be bound chemically (by aluminates) and physically (by absorption on the pore walls). This removes them (temporarily or permanently) from the corrosion reaction.
- c. Some aggregates contain chlorides that cannot be leached into the pore water. They do not play any part in the corrosion threshold but will show up on acid soluble chloride ions.
- d. In very dry concrete, corrosion may not occur even at very high chloride concentrations as the water is missing.
- e. In saturated concrete, corrosion may not occur even at a very high chloride ion concentration as the oxygen is missing.

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Corrosion can be observed at 0.1% chloride in some cases and none seen >1.0% chloride by weight of cement or more in others. If (d) or (e) are the reasons that no corrosion is observed, then a change in conditions may lead to corrosion.

The failure analysis performed by Beta Laboratory revealed several facts:

- Chlorides were found on the surface of a corroded pit. The concentration of the chlorides by SEM was about 0.3% or 3,000 PPM. Even though this is a semi-quantitative analysis, an error of 50% would still result in sufficient chlorides being present to initiate the autocatalytic corrosion of steel in the presence of water and oxygen.
- The water leachable chlorides found in the two concrete samples were Non detectable and 0.56 ppm. These concrete samples were obtained from the concrete near the steel containment liner. Therefore, it is considered that the chloride content of these samples is higher than the concrete at the outer surface of the concrete. The chloride concentrations were determined with a specific ion electrode.
- Air voids were found in the concrete in contact with the exterior surface of the steel containment liner. These voids were approximately 1/16 to 1/8 inches in diameter.
- The corroded two areas had just a few pits of considerable depth while the majority of the corroded area was of a uniform corrosion.

DISCUSSION OF POTENTIAL CORROSION SCINARIOS

Some of the considerations in the evaluation of the observed corrosion of the exterior of the steel containment liner include:

- The concrete had been exposed to alternating conditions of wet and dry over the life of the plant.
- There have been 17 refueling outages since Beaver Valley Unit 1 began operation. During these refueling outages, the temperature of the air inside containment would have been inspected to have been cooler than during operation of the reactor. Thus, if the humidity outside of the steel containment liner was lower than the dew point of the air outside the steel containment liner then condensation of water may have occurred on the exterior surface of the steel containment liner.

APPENDIX C

OVERVIEW OF SELECTED CORROSION REFERENCES TO DETERMINE PROBABLE FUTURE CORROSION

The external area of the containment steel liner that is in direct contact with the exterior concrete was originally in a passive corrosion state. The pH range of the concrete would have been expected to have been 12.5 to 12.8. The depth of the concrete cover to the steel containment liner, therefore, has a significant bearing on the corrosion protection provided by the concrete to the contacted steel. In general terms, the thicker the cover, the longer the concrete provides protection to the steel.

It is possible for the protection provided by the concrete to be overcome by chloride contamination of the concrete. Chloride, when entering the concrete as a contaminant of the mix constituents, is mostly (about 90%) complexed within the cement matrix, and only a small percentage is free in the pore solutions. The present codes of practice ban the use of chloride-bearing additives and restrict the amount of chloride present in concrete. For normally reinforced concrete made with ordinary Portland cement, the concrete should not contain more than 0.4% chloride ion with respect to the cement content weight/weight.²⁹

An experiment was performed by Tompson³¹ for six months to determine the corrosion of standard reinforcing steel embedded in concrete. (This work is analogous to Beaver Valley containment steel liner because of the proximity of the concrete to the steel liner). A full matrix of experiments was performed for three chloride concentrations, three temperatures and three relative humidities. These data along with the test conditions are summarized in Table 12.

Table 4 shows the mortar A2 (a Portland cement concrete mix similar to that used at Beaver Valley Unit 1 and standard reinforcing steel type. This table is a summary of the experiments with concrete that contained three concentrations of chlorides. These concentrations were 252 ppm, 756 ppm and 2,520 ppm. The corrosion rates measured were generally quite low.³¹

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Table 4. Data for Mortar A2 and Conventional Reinforcing Steel Chloride Contaminated Concrete – Average Corrosion Rates.³¹

Temperature, °F	Relative Humidity, %	Chloride Concentration, ppm	Measured Corrosion Rate, Mpy
40	43	252	0.10
40	43	756	0.06
40	43	2,520	0.05
40	75	252	0.01
40	75	756	0.04
40	75	2,520	0.61
40	98	252	0.02
40	98	756	0.45
40	98	2,520	0.35
70	43	252	0.08
70	43	756	0.12
70	43	2,520	0.42
70	75	252	0.03
70	75	756	0.02
70	75	2,520	0.83
70	98	252	0.09
70	98	756	0.08
70	98	2,520	2.2
100	43	252	0.00
100	43	756	0.01
100	43	2,520	0.03
100	75	252	0.04
100	75	756	0.01
100	75	2,520	0.07
100	98	252	0.03
100	98	756	0.56
100	98	2,520	13.

In conclusion, these experiments show that higher chloride concentration in the concrete, higher temperatures, and high relative humidity increase the corrosion rate of carbon steel materials.

LIMITATIONS AND CLARIFICATIONS

The conclusions and recommendations provided by this report are limited by and/or to the following:

- The containment liner integrity is acceptable and will remain acceptable if the recommendations in this report are implemented.

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- Implementation of the recommendations provided by this report will detect future possible corrosion if it occurs in the steel containment liner. Inspection of the interior coating on the steel containment liner is required to ensure the vapor tightness of the steel liner is maintained.

INCLUDE A DISCUSSION AND FIGURE OF OXYGEN CONCENTRATION CELL CORROSION

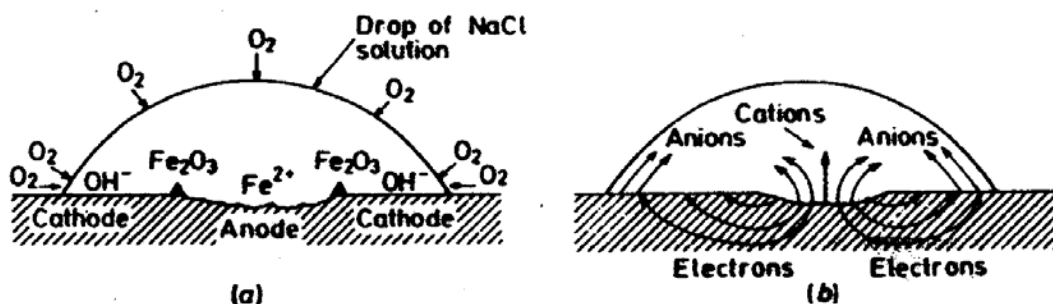


Figure 2. Oxygen Concentration Cell

A visual examination of the exterior surface of the removed section of containment liner revealed that part of the original mill scale was still present. Where the original mill scale had been removed outside of the corroded areas, there was only minor surface corrosion or flash rusting of the mill scale-free steel.

Corrosion had occurred in three roughly circular areas (comprising a total of 3 to 4 square feet) of the removed section of the containment steel liner. The majority of the pitting corrosion visually appeared to be oxygen concentration cell corrosion. There were several pits that contained black corrosion products. Since the high pressure water blasting would be expected to have removed all of the original corrosion products, these specific corrosion products are assumed to have formed after the steel had been water blast cleaned. An attempt was made to preserve these corrosion products for chemical analysis by Beta Lab. Two of the pitted areas of the removed carbon steel panel were submitted to Beta Lab for further metallurgical and corrosion analysis.

Disclosure Statement

Non site-specific corrosion-related technical reference material was taken from the report, "Davis-Besse Nuclear Plant, Engineering Assessment Report, Containment Vessel Corrosion, Prepared for FirstEnergy Corp., Safety-Related, SL-007564, Revision 1, April 2003, Sargent & Lundy, LLC, Chicago, IL 60603." Verbal authorization was received from Farid Berry March 1, 2006 to use portions of the referenced David Besse Report SL-007564, Revision 1, April 2003.⁴⁰

Attachment 10

Corrosion Evaluation Report

(21 pages)

Inputs: SGRP NRC 044
Beta Lab Report M06074
Corrosion Evaluation –Eldon Dille
Rebar Photos and Inspection

Writer's Note: All photos, table and figures attached will have a CE-xx designator, since this report is a sub-report to a larger overall effort

The Beaver Valley Steam Generator Replacement Project NCR No. 044 identified a corrosion pitting condition on two (2) locations of approximately a foot square each on the 17 1/2 ft. by 20 ft. piece of Containment Liner plate removed to provide access for the replacement activities (See Figure CE-1). After removal a third less pitted area was identified. This third area displayed less corrosion damage and is therefore bounded by this evaluation. The remaining surface of the liner plate displayed slight surface corrosion associated with the water blasting. The original two (2) locations were removed by site personnel and sent to Beta Laboratory for performance of investigative testing. (Figures CE-2A and CE-2B)

The corroded areas visually appear to be pitting in the carbon steel liner plate on the surface adjacent to the concrete indicative of general pitting and corrosion wastage, typical of an oxygen concentration cell type corrosion. The corroded surface areas were found following water blasting of the concrete, thus none of the corrosion product on the surface of the areas in question remained for investigation (Reference Figures CE-3A and CE-3B). Due to the lack corrosion product following the concrete removal process, it can not be determined with certainty when the corrosion occurred, how long the corrosion process was active or if a corrosion catalyst was present.

Photos taken of the rebar removed from the exposed liner plate area were the virtually free of corrosion. One area approximately nine (9) inches in length displayed pitting corrosion and mechanical abrasion. Figures CE-4A thru 4C display the general condition of the Rebar and Figures 4D thru 4E show the area of corrosion and damage identified on the one piece of rebar found to have damage. As can be seen from Figure 4E, the corrosion pitting area is small with the most significant damage coming from a mechanical abrasion. The damage, corrosion and mechanical, was confined to a nine (9) inch long region of one bar. The conclusion that can be drawn from this is that the general environment around the steel rebar (the concrete) is not a corrosive environment.

From the Beta Laboratory report, M06074, the following summary statements can be made:

- No unusual materials were identified as present in the corrosion product trapped in pits thought to most likely be protected from the water blasting concrete removal process. Figures CE-5A and CE-5B (Figures 14 and 17 from the Beta report) show the pit that was examined and Figure CE-5C (Table 4 of the Beta report) is the table of elements found in all the pits examined
- The concrete did display small void spaces at the concrete to liner interface. Figure CE-6 (Figure 7 from the Beta report).
- The concrete was of a high pH value – in excess of 10.5 which would be non-corrosive to the steel liner plate and rebar.

- The chemistry of the steel liner plate was within the specification values for ASTM A516, which is the specified material for the liner plate.
- Very low levels of chlorides (< 1 ppm) were found on the concrete pieces. The source of the chlorides is unknown for fact. However the water used in the concrete removal process and a decontaminate used by Health Physics to clean a piece of the concrete did contain low levels of chlorides.
- A low level of chlorides was identified on the surface of the liner plate, no concentration of chlorides was detected in or around the periphery of the corrosion products tested and the affected area showed no preferential location of the chlorides (it was evenly distributed across the surface). A source of these chlorides could not be identified.
- Pit depths of nearly 7/23 inch were identified in a liner plate with a nominal thickness of 3/8 inch. Therefore the pit depth was slightly over 50% thru wall
- A weld in the area of pitting corrosion exhibited corrosion across the weld, thus dating the corrosion to a time after the weld was made during construction. Additionally no preferential corrosive attack was observed at the weld heat affected zone or on the weld itself. See Figure CE-3A
- As can be seen in Figure CE-3A, there appears to be the outline of possible foreign matter that was trapped between the concrete and steel. Examination of the area found no detectable difference in the corrosion deposits that remained following water blasting.

Based upon the investigation data provided in Beta report M06074 and the information on concrete/steel corrosion provided in the report provided by Specialists In Solutions, Inc., the following conclusions are drawn concerning the corrosion activities:

- The corrosion is general pitting corrosion (wastage) with no evidence of stress corrosion or microbiological attack. The metallographic work performed by Beta Labs found the pitting to rounded in nature with no crack like projections. The examination of the corrosion product trapped in the deep pits identified no usual levels of elements that were not expected to be present. No preferential corrosion attack was observed on the sample piece with the weld or on the welds around the Nelson studs welded to the liner plate (Figure CE-8). Some crevice corrosion was observed in the cross section of the studs where the flash would trap contaminants (Figure CE-9).
- The corrosion occurred after welding and construction of the liner plate since the corrosion pitting was even across the weld, the heat affected zone (HAZ) and both edges of the weld where weld prep would have occurred.
- An abundant supply of the necessary elements for corrosion (oxygen and water) was present throughout the construction phase which lasted for nearly a year. This would be the timeframe from the fabrication and erection of the liner plate and completion of concrete pours for the top of the containment structure. During this timeframe water in the form of the wetting methodology used during the concrete pour sequences and weather (rain and snow) could accumulate in areas between the liner plate and the concrete structure. Corrosion activities are likely to have initiated at this time.
- Access to these necessary elements for corrosion activity became significantly limited once the concrete structure was completed. Exposure to water sources all but ceased and the concrete/steel interface was no longer exposed to the atmosphere for re-oxygenation. It should be noted that cracks in the concrete can

provide a path for the introduction of these constituents through a very torturous path in the concrete. These pathways would be largest during pressurized testing of the containment structure. These pathways are not believed to be a viable means of obtaining significant re-introduction of water and oxygen.

- The corrosion process consumes oxygen and once it is depleted corrosion can not be sustained at a high rate due to the limited supply of oxygen in the narrow annulus between the concrete and the liner plate following fabrication.
- No corrosive agents or corrosion catalysts, such as chlorides, could be identified on or in the steel liner plate, corrosion products remaining in the pits or the concrete materials tested in concentrations that would be of concern. However, it must be considered that such materials may have existed in local areas and were removed during the water blasting process.
- Approximately 1% of the observable liner plate contained corroded areas and a smaller percentage of the rebar surface area had evidence of corrosion, it is reasonable to assume that the concrete did not contain corrosive agents and that corrosion elements (water and oxygen) were not present in abundant amounts. It must also be noted that the rebar and liner plate were located in a vertical section of the containment structure. Being in the vertical position would make these locations unlikely locations for water and oxygen to enter the structure.
- The corrosion is localized for reasons that can not be determined with certainty. However, small breaks in the mill scale surface or other surface imperfections can provide the initiation sites for pitting (oxygen cell corrosion), as noted in the Corrosion Study by Specialists In Solutions, Inc.
- Figure CE-6 identified that the concrete did contain small void areas at the concrete/steel interface. These voids would most likely have filled with water during the construction phase. During the post-construction life of the liner, these locations could also serve as an accumulation point for any moisture that enters the concrete structure. It should also be noted that the area of the containment liner where the concrete was found to have small voids at the steel/concrete interface was removed; revealed no corrosion activity.
- It is possible that during the construction process contaminants could have been introduced at random locations. Organic material such as gloves, wood, paper, food product and waste may have been introduced during the work activity since strict Foreign Material control was not part of the normal work practice of the day. These types of products have been identified by other power plants that removed the liner plate from the inside of containment leaving the concrete in place. The foreign debris was identifiable since the corrosion product was available for analysis. In our case little or no corrosion product remained following the water blasting.

As noted in the Corrosion Assessment provided by Specialists In Solutions, Inc, the primary source of passivation of the steel used in fabrication of the containment liner, studs and rebar is the passivating properties of concrete, itself. The passivity of the steel depends upon the quality of the concrete in contact with the steel and the intimate contact of the steel by the concrete. It was concluded that where the containment steel liner, studs and rebar are in contact with the concrete cover, the containment steel liner at Beaver Valley Unit 1 should be in a passivated state and not subject to oxygen concentration cell corrosion. The visual inspection of the removed cutout and rebar identified that the majority of the surfaces in contact with the concrete were passive to oxygen.

concentration cell corrosion mechanism. Figure CE-7 shows the highly irregular pitting pattern that may be associated with the void spaces in the concrete coupled with the accumulation of water and oxygen and small breaks in the mill scale on the liner plate which could lead to pitting (oxygen cell corrosion).

Conclusions:

From the laboratory data and the technical background provided in the Specialists In Solutions, Inc. report, it is most likely that the pitting corrosion initiated during the construction period and then slowed as the available oxygen and water were consumed. It is possible that periodic wetting re-occurred during refueling periods and small amounts of oxygen could be introduced during the containment testing activities when the crack width would have been widest due to the expansion of the containment during the testing evolution. Another potential source for the re-introduction of aerated moisture would be the saturation of the non-vertical sections of the containment structure where environmental sources of fluids would be in contact with the cracked surfaces for extended periods of time. The introduction of moisture through cracks would require the complete through wetting of the concrete and a 100% relative humidity in the atmosphere. Once the atmosphere would be less than 100% relative humidity the moisture in the concrete would evaporate to establish an equilibrium condition with its environment.

It is expected that the current and future corrosion rates would be low due to the expected low level of oxygen available at the liner/concrete interface. The corrosion of the rebar should self-identify through spalling at the corrosion location (most likely at the exterior surface) due the corrosion product stresses introduced on the concrete. Corrosion of the liner would be expected to self-identify on the painted interior surface of containment as stained (rusty looking) protruding (bulged or flaking) areas on the painted surface.

The corrosion observed on the liner can not be assumed to be specific to the locations identified since the initiators could not be identified. This type of corrosion may occur at random locations of structures with this configuration and would most likely have slow corrosion rates. Monitoring the surface conditions, both interior and exterior, for early evidence of corrosion activity is highly recommended. Additional assurance measures should be assessed.



Figure CE-1

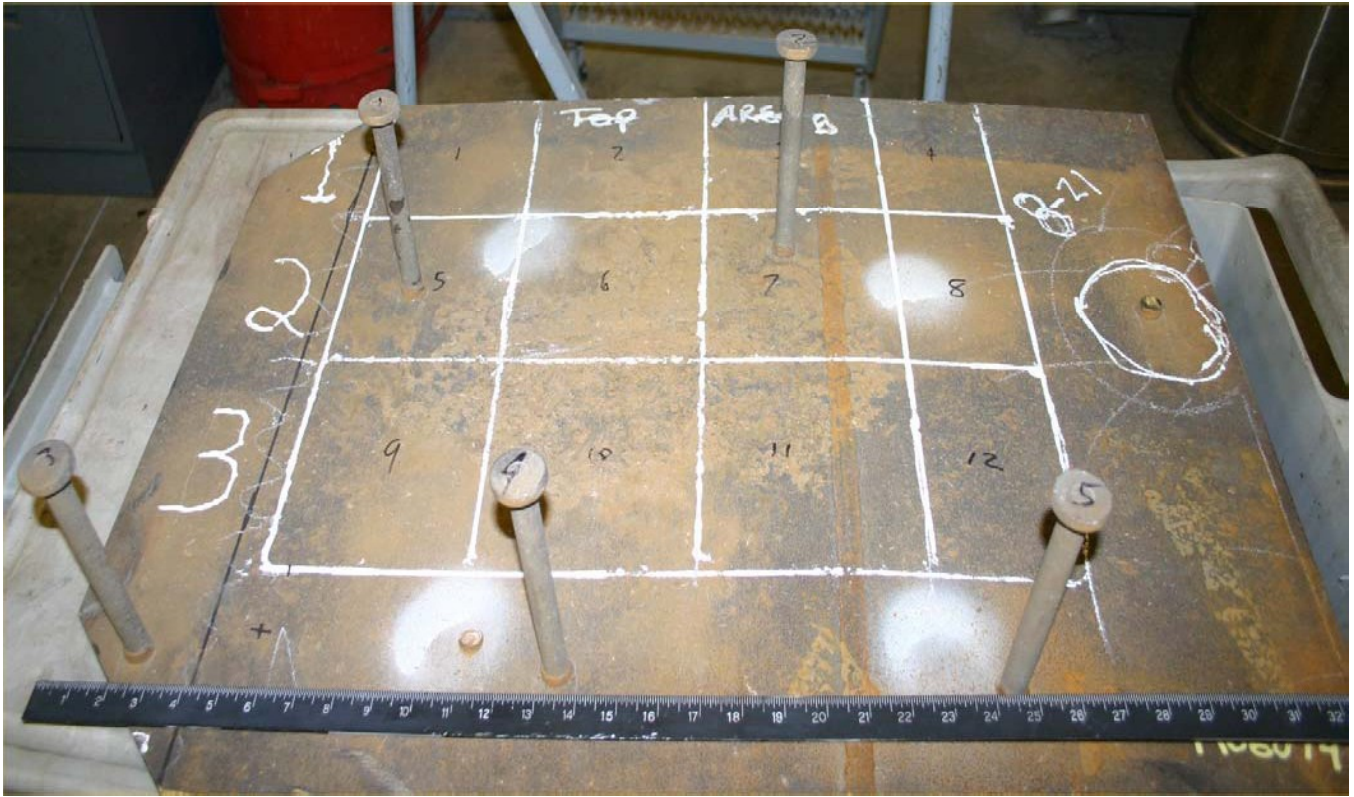


Figure CE-2A

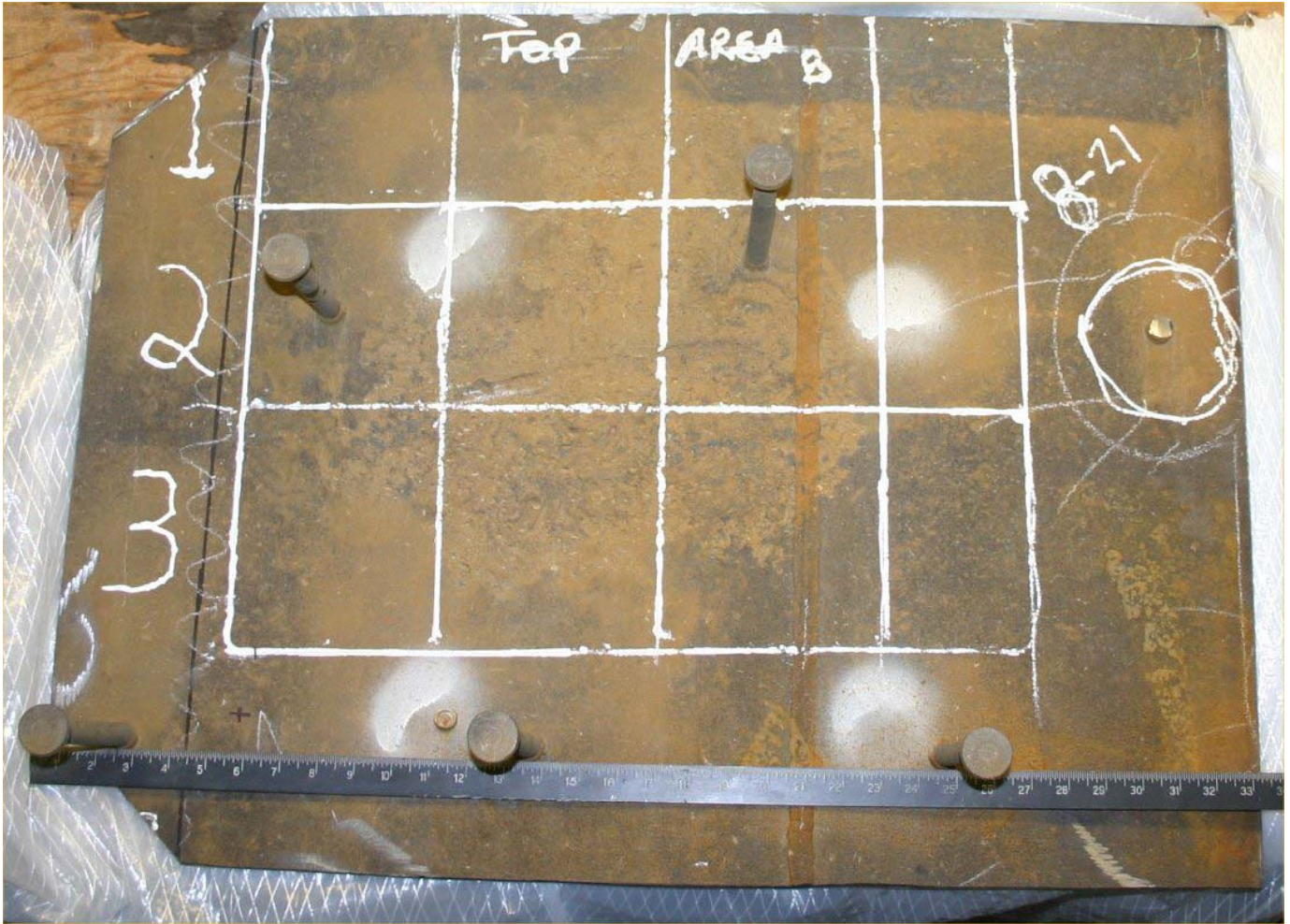


Figure CE-2B



Figure CE-3A



Figure CE-3B



Figure CE-4A



Figure CE-4B



Figure CE-4C



Figure CE-4D



Figure CE-4E