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**Metallographic Examination of
Surveillance Coupons from the
Wilsonville, Alabama, Solvent
Refined Coal Pilot Plant, 1977-1978**

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MASTER

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METALS AND CERAMICS DIVISION

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V. B. Baylor, R. T. King, B. C. Leslie, R. S. Crouse,
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V. B. Baylor, R. T. King,^{*} B. C. Leslie, R. S. Crouse,
A. J. Patko,[†] and K. C. Taber[‡]

ABSTRACT

Commercialization of the solvent refined coal (SRC) process requires corrosion-resistant yet economical materials of construction. A corrosion surveillance program was initiated at the Wilsonville, Alabama, SRC pilot plant to expose racks of welded specimens of engineering alloys to the various process conditions in major plant vessels. To observe the long-term cumulative exposure effects, sections were taken from the specimens after six months. The coupons were replaced in the vessels for another year and then reexamined. These sections were evaluated at ORNL by standard procedures. Microprobe analyses were performed on the scale on selected specimens. The scale, both on and below the surface, proved to be varying complex mixtures of oxides and sulfides sometimes intermixed with process stream material. Weight change records indicate that corrosion was not a serious problem during these exposures, with the coals processed to date.

INTRODUCTION

The conversion of coal to produce clean-burning fuels has been demonstrated to be technically feasible by the Solvent Refined Coal (SRC) process. A 6 ton/d[‡] SRC pilot plant in Wilsonville, Alabama, and a 50 ton/d[‡] SRC pilot plant at Fort Lewis, Washington, have been operated since 1974, producing low-sulfur, virtually ash-free products from coal.^{1,2} The Wilsonville plant was designed and constructed by

^{*}Formerly with ORNL, now with Sprague Electric Co., North Adams, Mass.

[†]Catalytic, Inc.

[‡]Nameplate capacities; 1 ton = 907 kg.

Catalytic, Inc., who operates it under management of Southern Company Services, Inc., under sponsorship of the Department of Energy (DOE) and the Electric Power Research Institute (EPRI).

Coal is processed at the Wilsonville plant by slurrying pulverized coal with process-derived solvent and heating to 416–460°C (780–860°F) under hydrogen pressure of 11.7–16.6 MPa (1700–2400 psig).¹ These conditions promote the hydrocracking of the coal molecular structure and the removal of sulfur by the formation of hydrogen sulfide. The reaction product is separated, filtered, and further fractionated to form light organic liquids, wash solvent for the filtration system, recycle process solvent, and liquid SRC, which is solidified by cooling.¹

Scale-up of the SRC process to commercial size demands materials of construction with long-term resistance to corrosion. Although erosion has been the most publicized problem at the SRC pilot plants, streams lacking solids have contributed to metal wastage through corrosion, particularly in the fractionation areas.^{3,4} In order to investigate the possibility of corrosion damage, Catalytic began a program to expose surveillance coupons of important engineering alloys to plant conditions. Coupons have been exposed since 1974 in most of the major process vessels. The racks of specimens we examined were inserted in March 1977 and were removed in September 1977. Specimens were sectioned and replaced in the vessels to accrue further exposure. They were removed again in September 1978. Sections of these specimens were examined at Oak Ridge National Laboratory (ORNL) by standard metallographic procedures and electron microprobe analysis to determine the extent and nature of the corrosion during each exposure period.

PROCESS DESCRIPTION

A simplified flowsheet of the Wilsonville SRC pilot plant is shown in Fig. 1. In the V-101A Slurry Blend Tank, pulverized feed coal, 95% of which is typically 200-mesh or smaller, is mixed with process-derived solvent, which has a boiling range of 232–482°C (450–900°F). Gas containing 85% H₂ by volume is fed to the slurry, and the mixture is then

heated to 400–450°C in the B-102 Slurry Preheater before flowing into the R-101 Dissolver, where a residence time of 30–60 min at 400–450°C allows the coal to react.

The slurry flows next to the V-103 High Pressure Separator, where the vapor is separated from the slurry. The vapor from the separator is cooled and again separated in the V-104 High Pressure Vent Separator. The V-104 vapor phase consists primarily of hydrogen sulfide, hydrocarbon gases, and unreacted hydrogen. The liquid phase includes water and organic compounds. The liquid condensed by cooling after the V-103, primarily water and organic compounds, flows to the V-105 Solvent Decanter, where the organic liquids are separated.

After pressure reduction, the slurry from the V-103 is sent to the V-111 Reclaim Tank. Liquid from the reclaim tank is filtered to remove the ash, unreacted coal, and other solid particles. The filtered solution is fed to the T-102 Vacuum Column, which distills the solution into various organic fractions. The bottoms from T-102 are drawn off and cooled to form solid SRC. The wash solvent and recycle process solvent are drawn from two trays in the column, combined and sent to the T-105 Fractionation Column. The overhead vapors are later condensed and fed to the T-104 Light Solvent Recovery Column, along with the organic liquid from the V-105 Solvent Decanter. Those liquids that boil at 177°C (350°F) or higher are fed back to the T-102 for further separation. Some wash solvent from the T-102 and the process solvent are pumped to the T-105 Solvent Fractionation Column, where wash solvent, which boils between 177 and 232°C, is separated from recycle process solvent. Both are then sent to storage tanks for use in filtration and slurring, respectively.

SURVEILLANCE COUPON PROGRAM DESCRIPTION

Figure 2(a) shows the configuration used in mounting racks of coupons in the various process vessels. Typically a 16-mm (5/8-in.) nut is welded to a blind flange, bolted cover, or nozzle in one or more locations in a vessel. Corrosion specimens are mounted on a 16-mm (5/8-in.) rod threaded on both ends and are secured by a nut on one end. The assembly is inserted into the vessel by screwing the other end into the nut previously

TEST ASSEMBLY

DIMENSIONS IN
MILLIMETERS (INCHES)

TEST COUPON

Fig. 2. Test Assembly and Typical Coupon Section for Wilsonville SRC Plant Surveillance Program.

welded to the vessel. The specimens are electrically insulated from the rod and from each other by coating the rod and the spacers with ceramic material. Typically, the specimens are disks, 76 mm in diameter, 3.2 mm thick with a hole in the middle. They contain a diametral weld, as illustrated in Fig. 2(b). Welds are made by either the shielded metal-arc process with a covered electrode or the gas tungsten-arc process.

The specimen rods are of various lengths depending on vessel dimensions and contain from three to nine specimens each. Some are hung vertically and others horizontally. The coupons are exposed to vapor phase, to liquid phase, or to the vapor-liquid interface. Details from plant records on coupon location, sample material, and pertinent process conditions, as well as they are known, are shown in Table 1. Composition specifications for coupon materials are listed in Table 2.

One surveillance coupon rack was placed in each of the following vessels: R-101 Dissolver, V-103 High Pressure Separator, V-105 Solvent Decanter, V-111 Reclaim Tank, and V-178 Light Solvent Surge Tank. Two racks were inserted into the T-102 Vacuum Column and three racks were placed in the T-105 Fractionation Column. The program originally was planned to include the V-110 Flash Tank and the V-120 Filter Flash Feed Drum; however, no coupons were inserted in these vessels during the first two exposures. Coupons were inserted on March 4, 1977, in all vessels except the T-105 Fractionation Column; which had specimens inserted on May 16, 1977. All racks were removed September 12, 1977. Actual exposure times, when the plant was operating normally, were calculated to be 2350 h for the T-105 coupons and 4015 h for all others for the first exposure period. The specimens were reinserted in September 1977 and removed in September 1978 after accruing an additional 5730 h of exposure time.

Two types of coal were processed during the first exposure, Emery coal from Utah and Indiana V. Processing of the Indiana V coal continued during the second exposure. The compositions varied between the two coals, as did the compositions of the resultant SRC product as shown in Table 3. Because of the different coal chemistries and the frequently changing operating conditions, it is difficult to pinpoint the exact nature and contents of the vessels of interest over a given period. Not only were samples not taken from some locations of interest, but analyses

Table 1. Summary of Corrosion Coupons Exposed at Wilsonville SRC Pilot Plant
from March 1977 to September 1978

Vessel	Location	Test Coupon Material	Weld Material	Pressure	Temperature °C (°F)	Typical Contents (wt %)	
R-101 Dissolver	Bolted cover Vertical Vapor phase	316	E316-15	12-17 MPa	430-450	SRC	40-60 ^a
		347	E347-15	1700-2450	(805-845)	Organic liquid	5-25
		410	E410-15	psig		Water	3-8
		20 ^b	E320-15			Unreacted coal	5-25
		304	E308-15			Ash	7-12
		800	Inco Weld A			Hydrocarbon gases	4-12
		330	Inco Weld A			CO+CO ₂	1.0-4
		22-13-5	E312-15			H ₂ S	0.5-4
		26-1	GTA 26-1				
V-103 High Pressure Separator	Nozzle Horizontal Vapor phase	26-1	GTA 26-1	Same as R-101 dissolver	310-340 (590-650)	Same as R-101 dissolver	
		304L	E308L-15				
		316	E316-15				
		410	E410-15				
		22-13-5	E312-15				
V-105 Solvent Decanter	Nozzle Vertical Liquid-vapor interface	1018 CS	E6010	0.17 MPa	38	Ammonia	
		304L	E308L-15	10 psig	(100)	Organic liquid	
		410	E410-15			Decanter oil	
						Decanter water	
						Vent gas	
V-111 Reclaim Tank	Nozzle Horizontal Liquid phase	1018 CS	E6010	0.90 MPa	260-315	Cresol insolubles	7-14
		304L	E308L-15	115 psig	(500-600)	Ash	2-6
		410	E410-15			SRC	16-25
						Distillate	65-70

Table 1. (Continued)

Vessel	Location	Test Coupon Material	Weld Material	Pressure	Temperature °C (°F)	Typical Contents (wt %)
T-102 Vacuum Column M1	Manway top Horizontal Vapor phase	1018 CS 304L 410	E6010 E308L-15 E410-15	2-27 kPa 0.3-3.9 psia	93-102 (200-215)	Product Overhead light solvent Wash solvent Recycle process solvent
T-102 Vacuum Column M2	Manway bottom Horizontal Vapor phase (maybe liquid)	1018 CS 304L 410	E6010 E308L-15 E410-15	See above for overhead pressure	300-325 (590-615)	
T-105 Fraction- ation Column M1	Manway top Horizontal Liquid phase	316 20 ^b 304L 321 330 410 1018 CS 800	E316-15 E320-15 E308L-15 E347-15 Inco Weld A E410-15 E6010 Inco Weld A	0.13-0.14 MPa 4-5 psig	190-220 (380-430)	Column feed: Light organic liquid 0-2 Wash solvent 15-30 Process solvent 60-85
T-105 Fraction- ation Column M2	Manway middle Horizontal Liquid phase	316 304L 321 410 1018 CS 800	E316-15 E308L-15 E347-15 E410-15 E6010 Inco Weld A	See above for overhead pressure	250-260 (480-500)	Overhead product: Light organic liquid 11 Wash solvent 81-85 Process solvent 4-8

Table 1. (Continued)

Vessel	Location	Test Coupon Material	Weld Material	Pressure	Temperature °C (°F)	Typical Contents (wt %)
T-105	Manway	316	E316-15	See above for overhead pressure	290-300 (550-570)	Bottom product:
Fraction-	bottom	304L	E308L-15			Light organic liquid 1
ation	Horizontal	321	E347-15			Wash solvent 2-5
Column	Liquid phase	410	E410-15			Process solvent 94-97
M3		1018 CS	E6010			
		800	Inco Weld A			
V-178	Manway	316	E316-15	0.90 MPa 115 psig	110 (230) Top 290 (560) Bottom	Wash solvent from T-102
Light	Horizontal	304L	E308L-15			
Solvent	Liquid phase	321	E347-15			
Surge		410	E410-15			
Tank		1018 CS	E6010			
		800	Inco Weld A			

^aDissolver content percentages based on moisture-free coal feed.

^bCarpenter 20Cb-3.

Table 2. Typical Specifications of Chemical Composition for Materials Used
as Corrosion Coupons in Weight Percent

Alloy	Cr	Ni	C	Mn	Si	P	S	Other	Fe
316	16-18	10-14	0.08	2.0	1.0	0.045	0.030	2.0-3.0 Mo	Bal
347	17-19	9-13	0.08	2.0	1.0	0.045	0.030	10x %C Nb+Ta	Bal
410	11.5-13.5		0.15	1.0	1.0	0.040	0.030		Bal
Carpenter 20Cb-3	19-21	32-38	0.07	2.0	1.0	0.035	0.035	2.0-3.0 Mo, 1.0 Nb+Ta, 3.0-4.0 Cu	Bal
304	18-20	8-10.50	0.08	2.0	1.0	0.045	0.030		Bal
800	21	32.5	0.05	0.8	0.5		0.008	0.4 Ti, 0.4 Al, 0.4 Cu	46
330	19	35	0.05	1.5	1.25				43
22-13-5	20.5-23.5	11.5-13.5	0.06	4-6	1.0			1.5-3.0 Mo, 0.2-0.4 N, 0.1-0.3 V, 0.1-0.3 Nb	Bal
26-1	25.0-27.5	0.20 ^a	0.010	0.40	0.40	0.02	0.02	0.75-1.50 Mo, 0.20 Cu, ^a 0.015 N	Bal
304L	18-20	8-12	0.03	2.0	1.0	0.045	0.030		Bal
1018 CS			0.15-0.20	0.60-0.90		0.040	0.050		Bal
321	17-19	9-12	0.08	2.0	1.0	0.045	0.030	5x %C Ti	Bal

^aNi + Cu ≤ 0.50.

Table 3. Chemical Compositions of Coal and Resultant SRC Product
Processed During Corrosion Coupon Exposures

Constituent	Analysis, wt %			
	April 1977-June 1977 (Emery Coal)		June 1977-Sept. 1978 (Indiana V Coal)	
	Feed	SRC	Feed	SRC
<u>Ultimate Analysis</u>				
Carbon	74-76	81-88	66-70	85-87
Hydrogen	5.1-5.5	5.1-5.9	4.8-5.0	5.7-6.4
Nitrogen	1.0-1.3	1.3-1.8	1.0-1.5	1.9-2.4
Chlorine	<0.01-0.12	<0.01-0.06	<0.01	<0.01
Sulfur	0.9-1.0	0.38-0.59	3.2-4.1	0.71-0.97
Ash	7.9-8.6	1.3-8.9	9.0-12.5	0.10-0.57
Oxygen	8.3-10.2	2.8-5.3	9.2-11.7	3.9-5.7
<u>Forms of Sulfur</u>				
Pyritic	0.19-0.29	<0.01-0.02	1.5-1.9	<0.01-0.22
Sulfate	<0.01-0.01	<0.01	0.03-0.04	<0.01-0.22
Sulfide	<0.01-0.03	<0.01-0.07	0.01-0.12	<0.01-0.08
Organic	0.58-0.82	0.34-0.50	1.3-2.1	0.47-1.2
<u>Proximate Analyses</u>				
Moisture	2.5-2.8		2.7-7.4	
Ash	7.9-8.6	1.3-8.9	9.0-12.5	0.10-0.57
Volatile Matter	37-42	33-55	35-37	35-50
Fixed Carbon	50-56	44-65	47-51	47-65

varied from run to run since each plant run usually involved some differences in pressure, temperature, residence time, equipment configurations, or other important variables from preceding runs.

After the specimens were removed, they were soaked in a clean organic solvent to remove residual process material and were then brushed to remove loose scale and other deposits. The coupons were shipped to ORNL for weighing and sampling and returned to Wilsonville for reinsertion. After the second exposure, all cleaning and weighing were performed at Wilsonville, and a part of each specimen was shipped to ORNL for examination. Cross sections taken perpendicular to the welds were mounted and polished for metallographic examination. Photomicrographs were taken in the unetched condition of two representative areas after the first exposure; one showing the thickest scale on the specimen and the other showing either the minimum scale thickness observed or a different kind of attack. Electron microprobe analysis was performed on the scale of selected coupons to determine the elemental compositions of the phases present. The probe can detect sulfur directly, but not oxygen. Scales containing only small amounts of or no sulfur are presumed to be primarily oxides. After the second exposure a single micrograph was taken of each coupon to document any significant changes.

RESULTS

The corrosion rate data shown in Table 4 indicate that during the exposure periods examined corrosion was not particularly a problem. Most of the specimens outside the fractionation area had a corrosion rate below 0.01 mm/year. Even the coupons in the two vessels in the fractionation area (T-102 and T-105), where severe corrosion has been observed recently,⁴ were relatively unattacked (<0.25 mm/year) except for the carbon steel specimens, which exhibited rates of up to 0.83 mm/year. The corrosion rate data, however, may be somewhat misleading. As can be seen from the micrographs of the samples discussed below, quite a bit of corrosion scale is present on many coupons. Indeed, much of this scale was preserved for the purpose of this examination. As a result, the weight loss data are lower than they would be if all the scale had been removed.

Table 4. Corrosion Rates Calculated from Weight
Change Measurements for Corrosion Coupons
Exposed at the Wilsonville SRC Pilot
Plant, 3/77-9/78

Vessel	Material	Corrosion Rate, mm/year (mils/year)	
		3/77-9/77	9/77-9/78
R-101	316	0.05 (2.1)	0.04 (1.4)
	347	0.00 (0.0)	<i>a</i>
	410	0.10 (3.9)	0.03 (1.1)
	Carpenter 20Cb-3	0.01 (0.4)	0.01 (0.5)
	304	0.00 (0.0)	<i>a</i>
	800	0.03 (1.3)	0.04 (1.7)
	330	0.01 (0.3)	0.01 (0.2)
	22-13-5	0.00 (0.0)	<i>a</i>
	26-1	<i>a</i>	0.06 (2.2)
V-103	26-1	<i>a</i>	0.00 (0.0)
	304	0.02 (0.8)	0.01 (0.2)
	316	0.02 (0.6)	0.02 (0.6)
	410	<i>a</i>	0.03 (1.0)
	22-13-5	0.01 (0.3)	0.01 (0.2)
V-105	Carbon steel	0.02 (0.7)	0.00 (0.0)
	304	<i>a</i>	0.00 (0.0)
	410	0.00 (0.0)	0.00 (0.0)
V-111	Carbon steel	0.07 (2.9)	0.01 (0.2)
	304	0.00 (0.0)	<i>a</i>
	410	0.00 (0.0)	0.00 (0.0)
T-102(M1) (Top Manway)	Carbon steel	0.06 (2.3)	0.01 (0.2)
	304	0.00 (0.0)	0.00 (0.0)
	410	<0.11 (0.1)	0.00 (0.0)
T-102(M2) (Bottom Manway)	Carbon steel	0.65(25.7)	0.64(25.1)
	304	0.00 (0.0)	<i>a</i>
	410	0.01 (0.4)	0.01 (0.2)

Table 4. (Continued)

Vessel	Material	Corrosion Rate, mm/year (mils/year)	
		3/77-9/77	9/77-9/78
T-105(M1) (Top Manway)	316	0.00 (0.0)	0.00 (0.0)
	Carpenter 20Cb-3	0.03 (1.2)	0.00 (0.0)
	304	0.00 (0.0)	0.00 (0.0)
	321	0.00 (0.0)	0.00 (0.0)
	330	0.00 (0.0)	0.00 (0.0)
	410	0.01 (0.2)	0.00 (0.0)
	Carbon steel	0.05 (2.1)	0.03 (1.3)
	800	0.01 (0.2)	0.00 (0.0)
T-105(M2) (Middle Manway)	316	0.18 (7.0)	0.13 (5.2)
	304	0.18 (7.2)	0.04 (1.4)
	321	0.14 (5.6)	0.03 (1.0)
	410	0.21 (8.4)	0.06 (2.4)
	Carbon steel	0.23 (9.1)	0.08 (3.1)
	800	0.27 (10.5)	0.03 (1.3)
T-105(M3) (Bottom Manway)	316	0.01 (0.0)	<i>a</i>
	304	0.00 (0.0)	<i>a</i>
	321	0.03 (1.1)	
	410	0.13 (5.3)	0.05 (1.8)
	Carbon steel	0.77 (30.5)	0.83 (32.6)
	800	0.02 (0.8)	0.05 (2.1)
V-178	316	0.00 (0.0)	<i>u</i>
	304	0.01 (0.2)	0.00 (0.0)
	321	0.01 (0.3)	0.00 (0.0)
	410	0.01 (0.2)	0.00 (0.0)
	Carbon steel	0.12 (4.7)	0.07 (2.6)
	800	<0.01 (0.1)	0.00 (0.0)

^uSpecimen gained weight.

Fig. 3. Type 316 Stainless Steel Specimen Exposed for (a) 4015 Operating Hours and (b) an Additional 5730 h at the Wilsonville SRC Pilot Plant in the R-101 Dissolver.

We believe, however, even with complete scale removal, that the corrosion rates would not have been significantly higher. Since the purpose of this report is to discuss the scale characteristics, corrosion rate data will not be discussed further.

R-101 Dissolver

Photomicrographs of specimens from the R-101 Dissolver are shown in the following figures. The type 316 stainless steel (Fig. 3) shows surface scale and subsurface attack less than 25 μm (1 mil) thick; note the slight intergranular attack in Fig. 3(a) and the subsurface corrosion products in the welded region shown in Fig. 3(b). The type 347 stainless steel shows the same sort of attack as the type 316 stainless steel with slight intergranular attack [Fig. 4(a)] and with a dual-layer scale [Fig. 4(b)] about 70 μm thick with subsurface penetration.

The type 410 stainless steel (Fig. 5) has a multilayered scale, which is the thickest found on any of the dissolver specimens, ranging from 0.025 to 0.28 mm (1-11 mils). The outer layer is very irregular [Fig. 5(a)] with cracks throughout. The cracking and variability in scale thickness may be due to spalling of the scale or to the cleaning process. An irregular outer layer is shown also on the Carpenter 20Cb-3 section [Fig. 6(a)] with what appear to be several phases in the deposit. The subsurface attack is also irregular, and the deposits are of medium thickness relative to the other specimens. Some imbedded process stream material can be seen.

The deposits on the type 304 stainless steel (Fig. 7) are among the most interesting. Like the type 410 stainless steel, they show a great variation in thickness and appear as a multiphase scale adhering to a very irregular surface [Fig. 7(a)]. Figure 7(b) shows metallic inclusions imbedded in the dendritic scale structure near the weld, along with some subsurface attack.

Figure 8(a) shows subsurface attack and surface scale on alloy 800 with different appearances; these differences may be due to exfoliation or partial scaling followed by reexposure. The alloy 330 (Fig. 9) shows a darker deposit on the outer surface near the weld in Fig. 9(b) and some subsurface penetration. The deposit may be process stream material.

Fig. 4. Type 347 Stainless Steel Specimen Exposed for (a) 4015 Operating Hours and (b) an Additional 5730 h at the Wilsonville SRC Pilot Plant in the R-101 Dissolver.

Fig. 5. Type 410 Stainless Steel Specimen Exposed for (a) 4015 Operating Hours and (b) an Additional 5730 h at the Wilsonville SRC Pilot Plant in the R-101 Dissolver.

Fig. 6. Carpenter 20Cb-3 Specimen Exposed for (a) 4015 Operating Hours and (b) an Additional 5730 h at the Wilsonville SRC Pilot Plant in the R-101 Dissolver.

(a)

(b)

50 μ m

Fig. 7. Type 304 Stainless Steel Specimen Exposed for 4015 Operating Hours at the Wilsonville SRC Pilot Plant in the R-101 Dissolver. The specimen displayed similar subsurface penetration with less surface scale (probably removed during cleaning) after an additional exposure of 5730 h.

Fig. 8. Alloy 800 Specimen Exposed for 4015 Operating Hours at the Wilsonville SRC Pilot Plant in the R-101 Dissolver. After the second exposure of 5730 operating hours the extent of subsurface corrosion products had increased.

Fig. 9. Alloy 330 Specimen Exposed for 4015 Operating Hours at the Wilsonville SRC Pilot Plant in the R-101 Dissolver. After an additional 5730 h the specimen displayed the same general characteristics.

Figure 10(a) shows the interface between base metal and weld metal in the alloy 22-13-5. Some subsurface attack is noted after the second exposure [Fig. 10(b)], but the scale is thinner than on many of the dissolver specimens. The 26 Cr-1 Mo (Fig. 11) also shows evidence of subsurface corrosion products [Fig. 11(b)]. Note also the metallic inclusions from the process stream imbedded in the surface scale in Fig. 11(a), which probably account for the weight gain during exposure.

Microprobe analyses were performed on four of the coupons after the first exposure in the dissolver: types 304, 347, and 410 stainless steel and alloy 800. Figure 12 shows the analysis of the type 347 stainless steel. Area B [Fig. 12(c)] is an inner layer of scale, found to contain mostly chromium and iron with some sulfur and silicon. The outer layer appears to be sulfide, predominantly iron sulfide with some nickel sulfide. The presence of nickel is somewhat unexpected, since it is not present in the inner layer.

The composition of the scale on the alloy 800 (Fig. 13) shows some similarity to that observed for the type 347 stainless steel. The inner deposit is primarily chromium, iron, and sulfur with no nickel [Fig. 13(c)], yet the outer layer is predominantly nickel sulfide [Fig. 13(d)].

The presence of sulfides is quite evident in the type 410 stainless steel, as shown in Fig. 14. The inner scale is a somewhat homogeneous sulfide of iron and chromium [Fig. 14(c)] with stringers of primarily iron sulfide [Fig. 14(d)]. The outer layer is completely iron sulfide [Fig. 14(e)].

The complex scale on the type 304 stainless steel is analyzed in Fig. 15. The gray area that appears to be a subsurface deposit contains some sulfide [Fig. 15(c)], but the adjacent light gray area is all iron sulfide with no chromium present [Fig. 15(d)]. The outer surface contains dendrites of calcium-titanium in a matrix that contains calcium, silicon, titanium, and manganese [Fig. 15(e) and (f)]. These elements may be from the process stream or may be oxide spatter from the covered electrode used in welding.

Fig. 10. Alloy 22-13-5 Specimen Exposed for (a) 4015 Operating Hours and (b) an Additional 5730 h at the Wilsonville SRC Pilot Plant in the R-101 Dissolver.

Fig. 11. Specimen of 26 Cr-1 Mo Steel Exposed for 4015 Operating Hours at Wilsonville SRC Pilot Plant in the R-101 Dissolver.

(a)

Fig. 12. Microprobe
Analysis of Type 347 Stainless
Steel Specimen After Exposure in
the R-101 Dissolver.

(a)

Fig. 13. Microprobe
Analysis of Alloy 800 Specimen
Shown in Fig. 8(a) After Exposure
in the R-101 Dissolver.

(a)

(b)

(c)

(d)

(e)

Fig. 14. Microprobe Analysis of Type 410 Stainless Steel Specimen After Exposure in the R-101 Dissolver.

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Fig. 15. Microprobe Analysis of Type 304 Stainless Steel Specimen Shown in Fig. 7(b) After Exposure in the R-101 Dissolver.

V-103 High Pressure Separator

Those coupons exposed in the V-103 High Pressure Separator would be expected to resemble those in the dissolver since process conditions are similar, and to some extent this expectation is fulfilled. The 26 Cr-1 Mo steel shows imbedded metallic inclusions and subsurface corrosion products like those observed in Fig. 11. The type 304L stainless steel contains a multilayer, multiphase scale with an outer dendritic layer. The type 316 stainless steel surface deposits show the largest difference, with an outer layer that is not seen on the dissolver coupons; however, this layer may have been removed during cleaning of the dissolver specimen. The type 410 stainless steel specimen shows the same multistructured layers shown in Fig. 5 (p. 18) with some subsurface penetration in another location on the specimen. A relatively thin two-layer scale was observed again for the alloy 22-13-5.

V-105 Solvent Decanter

Specimens exposed in the V-105 Solvent Decanter exhibited mostly grain boundary or pitting attack; surface scales and deposits were relatively thin. The 1018 carbon steel shows a multilayer scale with what may be imbedded metallic inclusions and stringer-type penetrations up to 50 μm long. The type 304L stainless steel shows noticeable subsurface attack (predominantly pits about 100 μm deep) but no evidence of the thick dendritic-type outer scale noted previously. The attack of the type 410 stainless steel is characterized by many imbedded inclusions in a multiphase single layer on the surface and subsurface pits and stringer-type penetrations 30 μm deep.

V-111 Reclaim Tank

The attack on these same metals is quite different in the V-111 Reclaim Tank. The scale on the carbon steel (Fig. 16) is not distinctly layered but contains many different phases and some metallic particles. Subsurface penetration is also apparent [Fig. 16(b)] to a depth of about

50 μm

Fig. 16. Specimen of 1018 Carbon Steel Exposed for 4015 Operating Hours at the Wilsonville SRC Pilot Plant in the V-111 Reclaim Tank. After an additional 5730 h of exposure time the specimen exhibited a two-layer scale.

30 μm below the existing surface. The type 304L stainless steel has a different scale appearance (Fig. 17) when compared with the R-101 (type 304) and V-103 specimens; the scale is still multilayer but penetrates the surface more and contains inclusions not observed previously for this material. Intergranular penetrations were observed after the second exposure [Fig. 17(b)]. Figure 18 shows the extent of subsurface penetration in the type 410 stainless steel. Needle-like cracks extend from the multilayer scale. The subsurface penetration extended even further after the second exposure forming a layered corrosion product.

Microprobe analyses were performed on two areas of the carbon steel sample and on the type 410 stainless steel specimen. Figure 19 shows a two-layer surface deposit on the carbon steel separated by a banded region. The two layers have almost identical compositions, primarily iron sulfide [Fig. 19(c) and (e)], but the banded region contains substantially less sulfur with some chromium and silicon [Fig. 19(d)]. Another view of the scale on the carbon steel (Fig. 20) displays a pock-marked gray deposit containing Fe, Si, Mn, Ti, and Al, completely different from that observed in Fig. 19. These elements are present in trace quantities in the process streams or may be present as a result of weld spatter. The reaction product on the type 410 stainless steel (Fig. 21) is primarily iron and sulfur with a small amount of chromium [Fig. 21(c)]. As the scale penetrates the sample, the proportion of chromium present in the deposit increases substantially [Fig. 21(d)].

T-102 Vacuum Column

The following micrographs illustrate the deposits formed on carbon steel specimens in two locations in the T-102 Vacuum Column, one near the top (M1), where the temperature is considerably lower than that near the bottom (M2). There is also a difference in the ratio of vapor to liquid exposure, with more liquid exposure at the bottom (M2). From these two differences alone, one would expect the scale to be somewhat different on the two specimens, with the most damage occurring under the high-temperature liquid phase conditions. The amount of scale and depth of penetration are indeed different in the two locations in a comparison

Fig. 17. Type 304L Stainless Steel Specimen Exposed for (a) 4015 Operating Hours and (b) an Additional 5730 h at the Wilsonville SRC Pilot Plant in the V-111 Reclaim Tank.

50 μm

Fig. 18. Type 410 Stainless Steel Specimen Exposed for 4015 Operating Hours at the Wilsonville SRC Pilot Plant in the V-111 Reclaim Tank. Subsurface penetration increased during the second exposure period of 5730 h.

Fig. 19. Microprobe Analysis of 1018 Carbon Steel Sample Shown in Fig. 16(b) After Exposure in the V-III Reclaim Tank.

(a)

Fig. 20. Microprobe Analysis of 1018 Carbon Steel Sample Shown in Fig. 16(a) After Exposure in the V-III Reclaim Tank.

(a)

Fig. 21. Microprobe Analysis of Type 410 Stainless Steel Sample Shown in Fig. 18(b) After Exposure in the V-111 Reclaim Tank.

between Figs. 22 and 23; however, more subsurface damage and scale appear on the M1 specimen. Corrosion rate data for the two locations, however, are the same. Of particular interest is the relative degree of subsurface penetration. The M2 specimen has very little damage from penetration, but the subsurface scales in the M1 sample are multiphase and not only extend from the surface but appear as isolated pockets [Fig. 22(a)], possibly as a result of droplets condensing on the coupons. After the second exposure, the pitting is as deep as 130 μm (Fig. 24). The microprobe analyses (Figs. 25–28) show some similarity in composition of the surface deposits on the two specimens, as both are hypothesized to contain iron oxide [Figs. 25(c), 26(e), and 28(c) and (d)]. The scale is much more complex, however, on the M1 sample, both subsurface [Fig. 25(d)] and on the surface (Fig. 27). Subsurface sulfidation is shown in Figs. 25 and 26 below the iron oxide matrix containing dark areas with silicon and manganese [Fig. 26(c)]. In Fig. 27(c) through (f) varying amounts of these same elements along with small amounts of sulfur or titanium create complex deposits of differing composition and morphology.

The type 304L stainless steel also exhibits comparable differences in attack between the two exposure areas in the vacuum column. As in the carbon steel, the subsurface penetration found is deeper in the M1 sample (Fig. 29) than in the M2 specimen (Fig. 30). The M1 specimen after the second exposure [Fig. 29(b)] displayed pits containing corrosion products from which intergranular penetrations into the base metal were observed (up to 60 μm penetration). The multiphase surface scale has the same appearance on both coupons; however, unlike the carbon steel, the M2 specimen has more scale. Microprobe analyses of the reaction products on the type 304L (Figs. 31–34) show that the scale in most cases is probably an oxide of iron and chromium. In Fig. 31 the oxide on the M1 sample includes minor amounts of silicon, titanium, or manganese. The oxide also constitutes the M1 specimen subsurface reaction product (Fig. 32). A chromium-iron oxide also forms the corrosion deposit on the high-temperature specimen in one area of the sample (Fig. 33); however, the deposit on the other area of the M2 sample (Fig. 34) is a sulfide. Again note that nickel is not present in the innermost layer but is in the other two. The sulfide is much more predominant below the outer layer (as it was on the carbon steel sample), while the sample probably exhibits oxidation on the outer surface.

Fig. 22. Specimen of 1018 Carbon Steel Exposed for 4015 Operating Hours at the Wilsonville SRC Pilot Plant in the Top of the T-102 Vacuum Column (M1).

Fig. 23. Specimen of 1018 Carbon Steel Exposed for 4015 Operating Hours at the Wilsonville SRC Pilot Plant in the Bottom of the T-102 Vacuum Column (M2). The specimen did not change appearance noticeably after accruing an additional exposure time of 5730 h.

Fig. 24. Specimen of 1018 Carbon Steel Exposed for 9745 Operating Hours at the Wilsonville SRC Pilot Plant in the Top of the T-102 Vacuum Column (M1).

(a)

Fig. 25. Microprobe Analysis of 1018 Carbon Steel Sample Shown in Fig. 22(a) After Exposure in the Top of the T-102 Vacuum Column (M1).

(a)

Fig. 26. Microprobe Analysis of 1018 Carbon Steel Sample Shown in Fig. 22(b) After Exposure in the Top of the T-102 Vacuum Column (M1).

(a)

Fig. 27. Microprobe Analysis of 1018 Carbon Steel Sample Shown in Fig. 22(c) After Exposure in the Top of the T-102 Vacuum Column (M1).

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(a)

Fig. 28. Microprobe Analysis of 1018 Carbon Steel Sample Shown in Fig. 23 After Exposure in the Bottom of the T-102 Vacuum Column (M2).

(b)

(c)

(d)

Fig. 29. Type 304L Stainless Steel Specimen Exposed for (a) 4015 Operating Hours and (a) an Additional 5730 h at the Wilsonville SRC Pilot Plant in the Top of the T-102 Vacuum Column (M1).

50 μm

Fig. 30. Type 304L Stainless Steel Specimen Exposed for 4015 Operating Hours at the Wilsonville SRC Pilot Plant in the Bottom of the T-102 Vacuum Column (M2).

ORNL-DWG 80-11978

(a)

Fig. 31. Microprobe Analysis of Type 304L Stainless Steel Sample After Exposure in the Top of the T-102 Vacuum Column (M1).

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Fig. 32. Microprobe Analysis of Type 304L Stainless Steel Specimen Shown in Fig. 29(a) After Exposure in the Top of the T-102 Vacuum Column (M1).

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Fig. 33. Microprobe Analysis of Type 304L Stainless Steel Sample Shown in Fig. 30(b) After Exposure in the Bottom of the T-102 Vacuum Column (M2).

ORNL-DWG 80-11982

(a)

Fig. 34. Microprobe Analysis of Type 304L Stainless Steel Sample Shown in Fig. 30(a) After Exposure in the Bottom of the T-102 Vacuum Column (M2).

The type 410 stainless steel exposed to the Vacuum Column environment (Figs. 35 and 36) displays predominantly subsurface scale with some dendritic growth containing many small metallic inclusions [Fig. 35(b)]. An irregular surface layer is present on both the M1 [Fig. 35(a)] and M2 [Fig. 36(a)] samples; and, unlike in the previous coupons discussed, the subsurface attack is about the same in the M1 as in the M2 specimens. We observed stringers similar to those found on the type 410 specimen exposed in the V-111 Reclaim Tank (Fig. 18, p. 34). Figure 35(b) was taken near the weld, showing the dendritic deposits below the original surface. These deposits are revealed by microprobe analysis to be primarily titanium, possibly oxide, with varying amounts of Si, Ca, Cr, Mn, and K also present in the M1 scale (Fig. 37). Again, these elements may occur as a result of spatter from the welding operation. The outer layer at another location contains these elements with some calcium and iron also [Fig. 38(e)]. The inner layer and surface penetrations are discovered to be possible oxides of chromium and iron [Fig. 38(c) and (d)]. On the M2 specimen the same titanium plus other element oxide layer is also present as a dendritic deposit [Fig. 39(d)] but is accompanied by a band of iron sulfide with some chromium [Fig. 39(c)]. Another location on the sample showed sulfidation on the inner subsurface layer [Fig. 40(c)], and the outer layer is a possible oxide of iron and chromium [Fig. 40(d)] similar to that observed in Fig. 38.

T-105 Fractionation Column

Since the temperature range in the T-105 Fractionation Column lies between the two extremes of the T-102 Vacuum Column and the contents are similar, one would expect to find a similar type of corrosion behavior with increasing deposits and decreasing subsurface penetration as the temperature increases (M1 to M2 to M3, respectively). Figures 41 through 48 are photomicrographs of the coupons exposed to the lowest temperature (221–232°C) in the column (M1). In general, the surfaces of the specimens are relatively clean, particularly the type 316 stainless steel (Fig. 41), type 304L (Fig. 43), and alloy 800 [Fig. 48(a)]. The corrosion rate of the M1 specimens was less than 0.01 mm/year for most specimens, the lowest

Fig. 35. Type 410 Stainless Steel Specimen Exposed for 4015 Operating Hours at the Wilsonville SRC Pilot Plant in the Top of the T-102 Vacuum Column (M1).

Fig. 36. Type 410 Stainless Steel Specimen Exposed for (a) 4015 Operating Hours and (b) an Additional 5730 h at the Wilsonville SRC Pilot Plant in the Bottom of the T-102 Vacuum Column (M2).

(a)

Fig. 37. Microprobe Analysis of Type 410 Stainless Steel Sample Shown in Fig. 35(b) After Exposure in the Top of the T-102 Vacuum Column (M1).

Fig. 38. Microprobe Analysis of Type 410 Stainless Steel Sample Shown in Fig. 35(a) After Exposure in the Top of the T-102 Vacuum Column (M1).

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Fig. 39. Microprobe Analysis of Type 410 Stainless Steel Specimen After Exposure in the Bottom of the T-102 Vacuum Column (M2).

Fig. 40. Microprobe Analysis of Type 410 Stainless Steel Sample Shown in Fig. 36(a) After Exposure in the Top of the T-102 Vacuum Column (M2).

Fig. 41. Type 316 Stainless Steel Specimens Exposed at the Wilsonville SRC Pilot Plant in the Top of the T-105 Fractionation Column (M1). (a) After 2350 operating hours. (b) Similar intergranular penetrations seen after an additional 5730 h.

Fig. 42. Carpenter 20Cb-3 Specimen Exposed for 2350 Operating Hours at the Wilsonville SRC Pilot Plant in the Top of the T-105 Fractionation Column (M1). The specimen displayed the same general characteristics after an additional exposure of 5730 h.

Fig. 43. Type 304L Stainless Steel Specimen Exposed for (a) 2350 Operating Hours and (b) an Additional 5730 h at the Wilsonville SRC Pilot Plant in the Top of the T-105 Fractionation Column (M1).

Fig. 44. Type 321 Stainless Steel Specimen Exposed for 2350 Operating Hours at the Wilsonville SRC Pilot Plant in the Top of the T-105 Fractionation Column (M1). After an additional 5730 h of exposure time the specimen displayed attack in the welded area but otherwise appeared about the same.

(a)

(b)

50 μm

Fig. 45. Alloy 330 Specimen Exposed for 2350 Operating Hours at the Wilsonville SRC Pilot Plant in the Top of the T-105 Fractionation Column (M1). A cross section of the specimen after the second exposure period of 5730 h showed deep penetration in the weld.

50 μm

Fig. 46. Type 410 Stainless Steel Specimen Exposed for 2350 Operating Hours at the Wilsonville SRC Pilot Plant in the Top of the T-105 Fractionation Column (M1). The specimen exhibited increased subsurface stringer attack and the same scale characteristics after an additional exposure of 5730 h.

Fig. 47. Specimen of 1018 Carbon Steel exposed for 2350 Operating Hours at the Wilsonville SRC Pilot Plant in the Top of the T-105 Fractionation Column (M1). The depth of penetration on this specimen after an additional 5730 h of exposure had increased to 30 μm .

Fig. 48. Alloy 800 Specimen Exposed for 2350 Operating Hours at the Wilsonville SRC Pilot Plant in the Top of the T-105 Fractionation Column (M1). After an additional exposure of 5730 h the alloy 800 specimen appeared the same.

rate of any area in the column. A small amount of irregular scale containing metallic inclusions is noted on the alloy 330 [Fig. 45(a)] and alloy 800 [Fig. 48(b)]. Multiphase scale with the subsurface penetration is observed on the carbon steel (Fig. 47), Carpenter 26Cb-3 (Fig. 42), and especially on the type 410 stainless steel (Fig. 46), which has the greatest surface scale thickness and depth of penetration of any samples. Pits up to 100 μm deep and subsurface stringers [Fig. 43(b)] were found on the type 304L specimen after the second exposure period. Subsurface attack is also evident in the types 316 [Fig. 41(a)] and 321 (Fig. 44).

A second rack of specimens was exposed to a slightly higher temperature in the middle of the T-105 Fractionation Column (M2). The M2 specimens show greater surface attack and subsurface penetration than the M1 samples. The corrosion rates in this part of the column were higher than for any other area of any other vessel in which coupons were exposed. The type 316 stainless steel (Fig. 49) has a multiphase, multilayer scale deposit and pitting but shows none of the intergranular cracks noted for the M1 sample. The general attack is much greater on the type 304L in this area, with a multilayer scale on an irregular surface [Fig. 50(b)] with some evidence of surface penetration [Fig. 50(a)]. The subsurface attack is as deep on the type 321 M2 sample (Fig. 51) as on the 321 M1; however, the surface scale on the M2 sample is thicker and contains many phases along with what may be process stream material [Fig. 51(b)]. The process material layer also appears on the type 410 specimen [Fig. 52(a)] and the depth of the needle-like penetration is 150 μm after the second exposure period. Some pitting is observed on the carbon steel sample up to 40 μm deep [Fig. 53(a)] containing corrosion products with metallic inclusions.

The M2 alloy 800 specimen (Fig. 54) also displays greater subsurface penetration than does the M1 sample. Microprobe analysis performed on the M2 alloy 800 specimen (Fig. 55) shows the deposit in Fig. 54(a) to be a complex mixture of sulfides and oxides of chromium, nickel, and iron in a matrix of nickel-iron oxide. Figure 56 shows that the subsurface product in Fig. 54(b) is a result of extensive sulfidation. Of interest is that the dark band contains small amounts of many different elements [Fig. 56(e)] including silicon, aluminum, and titanium in addition to the

Fig. 49. Type 316 Stainless Steel Specimen Exposed for 2350 Operating Hours at the Wilsonville SRC Pilot Plant in the Middle of the T-105 Fractionation Column (M2).

Fig. 50. Type 304L Stainless Steel Specimen Exposed for 2350 Operating Hours at the Wilsonville SRC Pilot Plant in the Middle of the T-105 Fractionation Column (M2). After an additional 5730 h of exposure the specimen displayed the same general appearance.

Fig. 51. Type 321 Stainless Steel Specimen Exposed at the Wilsonville SRC Pilot Plant in the Middle of the T-105 Fractionation Column (M2). (a,b) Two views after 2350 operating hours. (c) The subsurface penetration increased during an additional exposure of 5730 h.

Fig. 52. Type 410 Stainless Steel Specimen Exposed for (a) 2350 Operating Hours and (b) After an Additional 5730 h at the Wilsonville SRC Pilot Plant in the Middle of the Fractionation Column (M2).

50 μm

Fig. 53. Specimen of 1018 Carbon Steel Exposed for (a) 2350 Operating Hours and (b) an Additional 5730 h at the Wilsonville SRC Pilot Plant in the Middle of the T-105 Fractionation Column (M2).

Fig. 54. Alloy 800 Specimen Exposed for 2350 Operating Hours at the Wilsonville SRC Pilot Plant in the Middle of the T-105 Fractionation Column (M2).

Fig. 55. Microprobe Analysis of Alloy 800 Sample Shown in Fig. 54(a) After Exposure in the Middle of the T-105 Fractionation Column (M2).

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(a)

Fig. 56. Microprobe Analysis of Alloy 800 Sample Shown in Fig. 54(b) After Exposure in the Middle of the T-105 Fractionation Column (M2).

predominant chromium-nickel sulfide. The adjacent gray area contains none of these elements but has significantly more chromium and sulfur, while the interior deposit appears to be mostly nickel sulfide.

The amount of subsurface penetration decreases considerably as expected for the samples exposed to the highest temperature range (M3) in the Fractionation Column. Some penetration or pitting is observed for all specimens; however, the magnitude is less than that observed for the M2 and, especially, the M1 specimens, with the exception of the type 316 stainless steel, which shows some cracking and pitting. In general, the surface scale appearance is similar to that of the other specimens, but the amount of multilayer oxide corrosion deposit is less than on both the M1 and M2 samples. The corrosion rates for most of the specimens in the M3 location were correspondingly low (<0.05 mm/year) except for the carbon steel and type 410 stainless steel specimens.

V-178 Light Solvent Surge Tank

Since the V-178 Light Solvent Surge Tank also contains wash solvent from the T-102, the coupons should exhibit some of the same characteristics as either the samples from the T-102 or those from the T-105. In general, the V-178 specimens do not show the same degree of subsurface penetration but have about the same amount of scale of the same general appearance as the T-102 and/or T-105 samples. For example, the multilayer deposit on the type 316 stainless steel resembles that shown in Fig. 49(a). As seen previously, the type 304L exhibits relatively little surface scale, with most damage being below the surface. The dendritic growth patterns in the type 410 corrosion deposit have been observed previously [Fig. 36(b), p. 53]. The scale on the carbon steel contains dark particles in a multilayer matrix. The alloy 800 is relatively unattacked; it exhibits a thin deposit containing metallic inclusions and process stream material with some subsurface cracks.

DISCUSSION

Since the purpose of the pilot plant is to investigate the process under varying conditions, the variation in process conditions within a

single vessel over a six-month interval may be quite large. Thus, these corrosion results cannot be related to variations in temperature, pressure, and other process variables. For example, while the coupons in the lowest temperature vessel (66°C) generally exhibited the least surface scale, these same materials exhibited a relatively large amount of scale at only a slightly higher temperature (93°C) in the Vacuum Column and relatively little scale (except for the type 410 stainless steel) at a much higher temperature (260°F) in the same vessel. Since any poorly adherent scale may have been removed by brushing, generalizations on corrosion based on surface scale thickness are difficult. The amount of surface scale also may mislead the corrosion rate determination and interpretation.

Some insight can be gained by studying the relative attack on materials as compared with their compositions. In the dissolver and the high-pressure separator, the materials that had the best overall resistance to surface scaling and subsurface attack were the alloy 22-13-5 and the alloy 26-1. These materials do not have many close similarities in composition, except for being slightly higher in chromium and containing more alloying additions (especially molybdenum) than the other materials tested. The behavior of the type 410 stainless steel was paradoxical; its surface corrosion deposit was among the thickest observed, yet it was relatively unattacked below the surface. Since the type 410 contains no nickel, which is known to be susceptible to sulfidation, then the degree of subsurface attack may be related to nickel content of the alloy in the dissolver and high-pressure separator.

Not surprisingly, in most locations where carbon steel was tested it proved to be among the least resistant materials to surface scale buildup; however, in general, it did not experience as much subsurface attack as did many of the more highly alloyed materials. The type 410 stainless steel was also among the least resistant alloys to both surface and subsurface attack in all locations except the dissolver and high-pressure separator. These two ferritic materials are the lowest in chromium (the carbon steel has none), the highest in carbon, and the only two materials tested outside the dissolver-separator area that contain no nickel. While the absence of

nickel in the dissolver-separator area may play a role in preventing sub-surface attack, in other areas of the plant the high nickel content of the material appears to be a major factor in corrosion resistance.

Corrosion rate measurements do not indicate corrosion to be a particular problem during the year and a half of coupon exposure. The highest corrosion rates were observed in the middle of the T-105 Fractionation Column for both time periods, yet these rates are within reasonable design allowances. While in general the austenitic stainless steels outperformed the ferritics (with the exception of 26 Cr-1 Mo in the dissolver), even the 1018 carbon steel performed acceptably in most locations during the two periods of exposure examined.

As a result of varying operating conditions coupled with gradients in process stream chemistry, the corrosion deposits found in this examination are quite complex, usually consisting of multiphase layers of oxides and sulfides. Because of the changing conditions determination of a single corrosion mechanism is not feasible, but the microprobe results reveal some interesting characteristics that warrant further investigation. For example, on the carbon steel sample exposed to the environment of the V-111 Reclaim Tank, the analysis of one area reveals an oxide deposit containing iron and trace elements from the process stream including, Mn, Si, Ti, and Al. They may be process stream trace elements or may have come from adjacent corrosion coupons. On another area of the same sample, the scale consists of two layers of iron sulfide (one penetrates the surface) sandwiching a layer containing sulfides and probably some oxides of iron, silicon, and chromium, the latter two of which are not contained in carbon steel. Why the scale varies so much from site to site on the sample and how the trace elements came to be in the middle of the iron sulfide deposit can perhaps be ascribed to changing process conditions during exposure coupled with scale exfoliation and weld spatter. For example, it may be hypothesized that the middle layer formed during shutdown while the plant was changing from processing the Emery coal to the Indiana V coal, and both coals cause the formation of sulfide. The number of layers, however, on the type 304L stainless steel coupon in the same tank suggests that this explanation is probably too simple.

The complex changes in scale composition and morphology from vessel to vessel are also not easily explained. For example, the process stream

in the fractionation area, specifically in the T-102 Vacuum Column and T-105 Fractionation Column, should contain little sulfur (mostly organic) and no active oxygen. The amount of oxidation that occurred, however, indicates the activity of oxygen to be unexpectedly high. It has been speculated that exposure of plant vessels to air during shutdown and/or possible air leaks could result in the presence of oxygen in the system at this point. The amount of sulfur reaching this area has ranged from 0.27 to 0.64 wt %.⁵ However, coal liquefaction streams containing 0.3 to 0.8% sulfur have caused sulfidation corrosion above 250°C.⁶ Thus, while some sulfidation may be expected (even though the temperature is low) the oxidation is surprising.

The behavior of alloying elements in forming corrosion product scales is also complex. For example, the tendency of the nickel and chromium to form oxides and/or sulfides relative to that of the iron was quite variable, as shown in the analysis of the alloy 800 specimen exposed to the middle (M2) of the T-105 Fractionation Column. In one region layers of primarily chromium and sulfur on the inside and one of chromium-nickel and sulfur, with trace elements from either the process stream or the metal, band a region containing virtually all nickel sulfide with no chromium. In another region on the same coupon the base metal near the deposit is very rich in nickel as is a chromium-free metallic phase at the surface. Between these two areas are two phases, one of predominantly nickel sulfide, with no chromium, and one of predominantly sulfur and chromium with no nickel. These observations attest to the variability of the process stream chemistry during the sample exposure and to the probability that the corrosion involves a sequence of oxidation-sulfidation reactions.

RECOMMENDATIONS

Recommendations below are based on two exposure periods of selected coupons, which may or may not be realistic materials of construction for future demonstration plants.

1. In the high-temperature, high-pressure areas (R-101 Dissolver and V-103 High Pressure Separator), the relatively high resistance to corrosion attack of the alloy 22-13-5 and the alloy 26-1 suggest that the most

resistant iron-base alloy for this application would be high in chromium (greater than 20%) and contain a variety of alloying elements, especially molybdenum. A high nickel content would not be advisable because of the potential for sulfidation.

Although the 26 Cr-1 Mo steel showed good corrosion resistance, it is a ferritic stainless steel and is therefore subject to a degradation in mechanical properties due to long exposure above 425°C. We recommend that this alloy not be considered as a material for pressure containment at this temperature and that this alloy would be more appropriately tested in the lower temperature areas of the plant.

Refinery experience dictates that the vessels for pressure containment in this region will more likely be a low-alloy steel (such as 2 1/4 Cr-1 Mo) overlaid with type 347 stainless steel or a duplex layer of types 309 and 347. Further testing of low-alloy ferritics and the stabilized austenitics is recommended.

2. In the lower temperature and pressure areas of the plant, the better corrosion resistance in this environment of type 304L over the stabilized austenitic stainless steels suggests that other alloys to test should include 316L and 317L as well as the high-nickel alloys such as Hastelloy G and perhaps a duplex ferritic-austenitic alloy. Other program additions could include alloys 801 and 825.

3. The above recommendations are based on corrosion resistance of the alloys and do not take into consideration the mechanical properties and freedom from fabrication sensitivity and stress corrosion cracking resistance necessary for these applications. A program is under way at ORNL to determine the susceptibility to stress corrosion cracking in coal liquefaction environments of some of these alloys. Mechanical properties testing in these environments has been limited.

SUMMARY

Welded coupons of various alloys were exposed to varying process conditions at the Wilsonville SRC pilot plant at ten locations in seven vessels. The temperature, pressure, and process stream compositions varied during the nominal six-month and one-year exposures. These variations dictate the general nature of all comments.

1. All exposed coupons had corrosion deposits, most being multiphase and multilayer with some degree of subsurface penetration. The specific characteristics of the scale, such as the composition and morphology of the phases, the adherence to the surface, and the thickness and/or depth of penetration varied not only from location to location and sample to sample, but even varied from one site to another on individual coupons.

2. Sulfidation and possibly oxidation were the primary mechanisms of scale buildup and penetration, and neither type of attack was particularly predominant. Oxides and sulfides were formed of iron, chromium, and nickel, sometimes containing trace elements, probably from the process stream or weld spatter. There was no pattern observed as to the number of layers and the order in which sulfidation and oxidation occurred.

3. High-chromium, molybdenum-containing alloys had the best resistance in the high-temperature, high-pressure areas of the plant and were not tested in other locations. In the other areas, the low carbon, higher nickel, and chromium steels performed best; those that were high in carbon, low in chromium, and free of nickel or alloying additions performed worst.

4. The depth of penetration, thickness of scale, and weight change measurements do not indicate corrosion to be an overwhelming problem after the first two exposures; however, varying process conditions may alter the corrosion resistance of these alloys considerably. The corrosion rates observed for the two exposures were similar with a few exceptions.

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