**CORROSION RESISTANCE AND BEHAVIOR OF CONSTRUCTION MATERIALS
EXPOSED TO DILUTE SULFURIC ACID AT ELEVATED
TEMPERATURES UNDER STATIC CONDITIONS**

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Abstract

Laboratory investigation has been undertaken to determine the electrochemical behavior and corrosion resistance of various construction materials in a simulated hydrolysis environment (5 wt% sulfuric acid) at temperatures ranging from 90 to 220°C. Tests were performed in an autoclave-type electrochemical cell. The corrosion behavior of the test materials was determined using computer-controlled DC potentiodynamic polarization. Corrosion rates of the test materials were determined using AC impedance techniques. Among the stainless steels tested, only alloy N08026 (Carpenter 20Mo-6) performed satisfactory up to a temperature of 100°C. The alloy passivated spontaneously in the environment and corroded at a rate of less than 2 mpy. None of the stainless steels tested could be used at 120°C or above. A number of nickel-based alloys tested had good corrosion resistance up to 100°C, but their corrosion rate exceeded 2 mpy at higher temperatures. Zirconium alloys were satisfactory up to 180°C. Only tantalum and a tantalum-niobium alloy were satisfactory up to 220°C.

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Introduction

Corrosion of construction materials for the hydrolysis reactor (hydrolyzer) is a serious problem because of the acid environment and elevated temperatures required for the reactions. In small-scale studies, only highly corrosion-resistant materials, such as zirconium alloys and tantalum, have been selected for the hydrolysis reactors and accessories. These refractory metals provide adequate corrosion performance in the hydrolysis environment, but their application is limited by their high cost and lack of availability. Currently, numerous high-chromium-nickel stainless steels and nickel-based alloys are available commercially at reasonable cost. However, existing data on corrosion resistance of these materials in the hydrolysis environment are inadequate, particularly at temperatures approaching and above the boiling point (100°C).

The objective of this study is to determine corrosion behavior of various construction materials exposed to a simulated hydrolysis environment (5 wt% dilute sulfuric acid at temperatures ranging from 90 to 220°C) by studying electrochemical potential-current relationships using DC potential polarization scan techniques. The general corrosion of test materials in the simulated hydrolysis environment was determined using AC impedance techniques. Results of the study provide basic information needed for proper material selection for hydrolysis reactors and associated equipment. The results also suggest that appropriate corrosion protection should be provided, if lower corrosion resistance, less-expensive materials are considered. Table 1 shows the compositions of the alloys, Unified Numbering System (UNS), trade name, and relative cost compared with stainless steel S31603 (TVA 1989). The passivity behavior of the alloys was studied using DC potentiodynamic polarization techniques (Liening 1986; ASTM 1992). General corrosion rates were determined using AC Impedance Spectroscopy (ASTM 1992).

Experiment

The test cell consisted of a PARR reactor constructed of stainless steel S31603. The cell interior was lined with 1/8-inch (0.32-cm) thick Teflon. The internal volume of the cell was approximately 2 liters. The cell was equipped with three identical electrode holders made of stainless steel S31603 and lined with Teflon for chemical and electrical insulation. One holder was used for the working electrode (test specimen) and it was located in the center of the cell. Two other holders were used for the reference and counter electrodes. They were located at the same level, on opposite sides, and 1.2 inches (3 cm) from the working electrode. All electrodes were electrically isolated from the test cell using alumina ceramics.

Test electrodes were designed and fabricated to conform with ASTM Standard G 3-89 (ASTM, 1992) and consisted of a 3/8-inch (0.95-cm) diameter and 0.5-inch (1.2-cm) high cylindrical specimen with a total exposed area of approximately 0.82 in² (5.3 cm²). The surface of the electrodes was machined to a 600-grit finish. The counter and reference electrodes were made of platinum. The tests (DC potentiodynamic and AC impedance) were conducted in accordance with ASTM Standard G 3-89. A 1-liter volume of fresh test solution was used for each test. The test solution was made using 98 wt% reagent sulfuric acid and distilled water to obtain a concentration of 5 wt%. The test specimen, counter, and reference electrodes were ultrasonically cleaned in actone, installed into the electrode holders, and then immersed in the test solution. The entire test cell was heated at an average rate of 1.5°C/minute using an electric furnace. The thermocouple was located at approximately the same level in the test cell as the test electrodes to ensure that the test temperature was uniform between these electrodes. The test temperature was controlled digitally within $\pm 3^\circ\text{C}$ from the temperature setpoint. After the test temperature was reached,

Table 1. Major Alloy Compositions of Construction Materials Exposed to 5 wt% Sulfuric Acid at Elevated Temperatures and Static Conditions

Matls tested	Trade Name	Composition, wt%											Cost ratio ^a
		C	Cr	Fe	Mn	Mo	Nb	Ni	Si	Ta	Zr	Other	
S31603	Type 316L	0.03	18	Bal.	2.0	3.0	-	12	1.0	-	-	-	1.0
N08904	Type 904L	0.02	23	Bal.	2.0	5.0	-	28	1.0	-	-	2.0Cu	1.4
N08020	Carp 20Cb-3	0.07	21	Bal.	2.0	3.0	1.0	38	1.0	-	-	4.0Cu	2.2
N08026	Carp 20Mo-6	0.03	26	Bal.	1.0	6.0	-	37	0.5	-	-	4.0Cu	2.3
N02200	Nickel 200	-	-	-	-	-	-	100	-	-	-	-	1.5
N04400	Monel 400	-	-	-	-	-	-	70	-	-	-	30Cu	2.0
N10665	Hast. B-2	0.01	1.0	2	-	28	-	Bal.	0.1	-	-	-	7.0
N08825	Incoloy 825	0.05	22	29	-	3.0	-	42	0.5	-	-	2Cu, 1Ti	2.3
N06030	Hast. G-30	0.03	30	15	-	5.5	0.8	43	1.0	-	-	2.5W	5.0
N08625	Inconel 625	0.10	22	5	-	9.0	4.0	62	0.5	-	-	-	2.3
N06022	Hast. C-22	0.01	22	-	-	10	2.0	53	-	-	-	3.0W	6.0
N10276	Hast. C-276	0.01	16	5.5	-	16	-	57	0.08	-	-	4.0W	6.0
R06702	Zr 705	0.05	<.2	<.2	-	-	-	-	-	-	95	4.5Hf	4.6
R06705	Zr 702	0.05	<.2	<.2	3.0	-	-	-	-	-	91	4.5Hf	4.6
-	KBI-40	-	-	-	-	-	40	-	-	-	60	0.3W	50.0
-	Tantalum	-	-	-	-	-	-	-	-	Bal.	-	-	120.0

^a a Relative cost ratio versus stainless steel S31603, Material Files, Muscle Shoals Corrosion Laboratory, National Fertilizer & Environmental Research Center, Alabama.

the test specimen was allowed to stabilize in the test solution for at least 30 minutes. The AC impedance test was then conducted for approximately 3 minutes. Next, the potentiodynamic polarization test was performed on the same specimen.

The AC impedance test was conducted using an EG&G Princeton Applied Research Model 378 electrochemical system and Model 388 AC impedance software. The polarization resistance, R_p , which is inversely proportional to the corrosion rate, was determined from the diameter of the Nyquist semicircle. The corrosion current density of the test specimen was calculated from the value of R_p by the following equations (Liening 1986; ASTM 1992):

$$I_{\text{corr}} (\mu\text{A}/\text{cm}^2) = x \cdot 10^6 \cdot B_a \cdot B_c / [2.3 \cdot (B_a + B_c) \cdot R_p \cdot A]$$

Where I_{corr} is corrosion current density, B_a and B_c are Tafel slopes, R_p is polarization resistance, and A is the exposure area of the specimen. Approximate values for Tafel slopes were selected to be equal to 100 mV for all test materials. The corrosion rate then can be calculated from the value of R_p using the following relationship (ASTM 1992):

$$\text{Rate (mpy)} = 2826 \cdot \text{EW} \cdot (dx \cdot A \cdot R_p)$$

Where mpy is mils per year, EW is equivalent weight, and d is alloy density. After AC impedance tests, anodic polarization tests were performed by scanning the surface potential of the test specimen from about -250 mV to 1600 mV versus the corrosion potential (E_{corr}), or to a current density of $10^4 \mu\text{A}/\text{cm}^2$, at a scan rate of 0.7 mV/s (0.6 V/hour). The test was conducted using an EG&G Princeton Applied Research Model 273 potentiostat and Model M342C electrochemical software in conjunction with a personal computer. Test data are presented in the form of specimen surface potential E (mV) versus specimen current density (A/cm^2) in semi-log scale. Passivity and corrosion behavior of the test materials were determined using the values of the corrosion potential (E_{corr}), the primary passivation potential (E_{pp}), the breakdown potential (E_b), the critical passivation current density (I_c), the passive current density (I_p), and the shape of the anodic polarizations curve.

Results and Discussion

For handling chemical media in which corrosion attack is uniform, metals are classified into four groups according to the uniform corrosion rate and intended application (ASM 1985; Fontana et al. 1970).

Excellent corrosion resistance: Metals corrode at rates of 2 mpy or less. These metals are normally specified for very critical components such as reactors. These metals are also selected for the conditions in which contamination of heavy metal ions may impair process reaction or lead to serious health hazards.

Good corrosion resistance: Metals corrode at rates of 2 to 5 mpy and are selected for critical components such as valves and pump shafts.

Fair corrosion resistance: Metals and alloys corrode at rates of 5 to 50 mpy. These metals are frequently selected for parts tolerable to some corrosion such as storage tanks, piping, pumps, and valve housings. Corrosion allowance is required to supplement for the loss of metal due to corrosion.

Severe corrosion of the hydrolysis reactor materials is not acceptable, because of the conditions of high temperature and pressure. In addition, high corrosion may cause serious contamination to the hydrolysis environment as well as to the downstream processes. Therefore, selection of materials for the hydrolysis reactors should be limited to metals with excellent corrosion rates of 2 mpy or less. For passive metals, the passivation should be stable (low critical and passive current densities) and spontaneous (metal corrodes in the passive range; the corrosion potential must be more noble than the E_{pp}). The passive current density should be equivalent to a corrosion rate not exceeding 2 mpy.

The AC and DC test results are listed in Tables 2 and 3. Figures 1 to 4 show examples of the DC potentiodynamic polarization of the test materials. Figure 5 shows the AC impedance data for the test materials.

Stainless Steels

At 90 and 100°C, results of the AC impedance tests showed that alloys S31603, N08904, and N08020 have poor-to-fair corrosion resistance (corrosion rate greater than 5 mpy, Table 2).

The potentiodynamic polarization scan tests revealed that all of these stainless steels exhibited stable passivation in 5 wt% sulfuric acid solution over a wide potential range (approximately 900 mV) and at low passive current densities $3 \mu\text{A}/\text{cm}^2$ or less). However, their passivation was not spontaneous. Therefore, these stainless steels were not satisfactory for hydrolysis service at either 90 or 100°C.

Because the passive current density of these stainless steels was about $3 \mu\text{A}/\text{cm}^2$ or less, an average corrosion rate of less than 2 mpy is achieved if these metals remain in the passive range. Examination of the DC potentiodynamic scan diagram revealed that these alloys corroded in the active range. The most stable corrosion potential recorded after the stabilization was more active than the primary passive potential (Table 2). In addition, several corrosion potentials were indicated by the shape of the polarization curves (Fig 1). This indicated that these stainless steels would corrode preferentially in the active or active-passive range. Passive corrosion is obtained on these stainless steels only when their corrosion potential potentiostatically polarized into the passive range. The initial current density required for complete polarization must exceed the alloy i_c (400-800 $\mu\text{A}/\text{m}^2$ for alloy S31603, 210-250 $\mu\text{A}/\text{cm}^2$ for alloy N08904, and about 300 $\mu\text{A}/\text{cm}^2$ for alloy N08020), but the current density required to maintain passivation is equal to i_p (between 2.5 and 3 $\mu\text{A}/\text{cm}^2$ for all three alloys). This technique is known as anodic protection.

Because of its higher molybdenum content, alloy N08026 showed superior corrosion resistance compared to alloys S31603, N08904, and N08020. At 90 and 100°C, the resistance to general corrosion of alloy N08026 was excellent. The alloy corroded at very low rates, 0.1 mpy at 90°C and 1 mpy at 100°C. The alloy exhibited spontaneous passivation, because the corrosion potential was more noble than the primary passive potential. The passive corrosion density

**Table 2. Results of Electrochemical Tests on Various Materials Exposed to
5 wt% Sulfuric Acid at 90, 100, and 1200C Under Static Conditions**

Matls tested	R _p Ohms	i _{cor} μA/cm ²	Cor.Rate mpv	E _{cor} mV/Pt	i _c μA/cm ²	i _p μA/cm ²	E _{sp} mV/Pt	E _p mV/Pt
<u>At 900C</u>								
S31603	19	204	79	-864	800	2.5	-750	90
N08904	39	25.4	10	-812	250	2.5	-710	190
N08020	126	30.8	12.0	-790	300	3.0	-710	290
N08026	3,500	1.1	0.4	-610	150	1.5	-660	290
N02200	139	22.9	12.0	-808	- ^b	- ^b	- ^b	- ^b
N04400	998	3.9	2.0	-761	- ^b	- ^b	- ^b	- ^b
N10665	2,000	2.0	1.0	-679	- ^b	- ^b	- ^b	- ^b
N08825	7,600	0.5	0.2	-571	- ^c	2.5	- ^c	290
n06030	41,000	0.1	<0.0	-521	- ^c	1.5	- ^c	290
N08625	6,900	0.6	0.2	-566	- ^c	3.0	- ^c	290
N06022	17,500	0.2	0.1	-542	- ^c	2.0	- ^c	190
N10276	12,000	0.3	0.1	-617	- ^c	1.0	- ^c	240
R60705	23,000	0.2	0.2	-637	- ^c	1.0	- ^c	- ^c
R60702	78,000	0.1	<0.1	-597	- ^c	1.0	- ^c	- ^c
KBI-40	41,000	0.1	0.1	-663	- ^c	1.0	- ^c	- ^c
Ta	100,000	0.0 ^a	<0.1	-658	- ^c	1.0	- ^c	- ^c
<u>At 1000C</u>								
S031603	15	258.8	100.0	-790	400	2.5	-712	263
N08904	100	38.8	15.0	-713	210	3.0	-678	163
N08020	80	48.5	19.0	-726	300	2.0	-637	263
N08026	2,300	1.7	1.0	-626	10	2.0	-637	363
N02200	19	204.3	88.0	-769	- ^b	- ^b	- ^b	- ^b
N04400	480	8.1	4.0	-703	- ^b	- ^b	- ^b	- ^b
N10665	900	4.3	2.0	-706	- ^b	- ^b	- ^b	- ^b
N08825	5,000	0.8	0.3	-526	170	3.0	-612	363
N06030	27,000	0.1	0.1	-535	- ^c	1.0	- ^c	363
N08625	6,000	0.6	0.3	-539	10	2.5	-637	313
N06022	18,000	0.2	0.1	-509	- ^c	2.0	- ^c	363
N10276	6,400	0.6	0.3	-512	- ^c	1.5	- ^c	363
R60705	25,000	0.2	0.1	-734	- ^c	1.0	- ^c	- ^c
R60702	33,000	0.1	0.1	-662	- ^c	1.5	- ^c	- ^c
KBI-40	51,000	0.1	0.1	-590	- ^c	1.0	- ^c	- ^c
Ta	63,000	0.0 ^a	<0.0	-691	- ^c	1.0	- ^c	- ^c
<u>At 1200C</u>								
S31603	2	2,588	1002.0	-289	4000	10.0	-250	300
N08904	60	64.7	26.0	-337	300	15.0	-325	400
N08020	30	129.4	51.0	-388	800	15.0	-375	450
N08026	160	24.3	10.0	-389	900	10.0	-450	300
N02200	10	338.2	166.0	-410	- ^b	- ^b	- ^b	- ^b
N04400	105	37.0	16.0	-265	- ^b	- ^b	- ^b	- ^b
N10665	120	32.4	15.0	-473	- ^b	- ^b	- ^b	- ^b
N08825	163	23.8	9.0	-309	100	10.0	-275	600
N06030	180	21.6	8.0	-329	105	9.0	-375	500
N08625	135	28.8	11.0	-250	200	10.0	-200	600
N06022	212	18.3	7.0	-289	2000	20.0	-500	550
N10276	270	14.4	6.0	-285	500	8.0	-350	400
R60705	9,000	0.4	0.4	-343	- ^c	2.5	- ^c	- ^c
R60702	11,500	0.3	0.3	-522	- ^c	2.5	- ^c	- ^c
KBI-40	22,500	0.2	0.1	-487	- ^c	2.0	- ^c	- ^c
Ta	22,000	0.2	0.1	-545	- ^c	1.5	- ^c	- ^c

^a Less than 0.1 ^b No passivation observed. ^c Outside measured range of potential. ^d Can not determine.

Table 3. Results of Electrochemical Tests on Various Materials Exposed to 5 wt% Sulfuric Acid at 140 to 220°C Under Static Conditions

Matls tested	R _p Ohms	i _{cor} μA/cm ²	Cor. Rate mpy	E _{cor} mV/Pt	i _c μA/cm ²	i _p μA/cm ²	E _{pp} mV/Pt	E _b mV/Pt
<u>At 140°C</u>								
N08904	0.23	16,578	6,646	-383	2000	100	-400	400
N08020	0.30	12,940	5,121	-329	- ^d	1000	- ^d	600
N08026	6	669	261	-344	800	20	-450	250
N4400	3	1553	674	-266	- ^b	- ^b	- ^b	- ^b
N10665	6	645	299	-267	- ^b	- ^b	- ^b	- ^b
N08825	5	746	296	-318	400	100	-100	300
N06030	16	243	91	-398	1000	50	-350	100
N08625	26	149	59	-306	100	50	0	400
N06022	12	323	129	-378	1000	100	-275	600
N10276	11	353	147	-336	2000	300	-250	400
R60705	12,000	0.4	0.4	-325	- ^c	3.5	- ^c	- ^c
R60702	16,000	0.3	0.2	-548	- ^c	2.5	- ^c	- ^c
KBI-40	25,000	0.2	0.1	-229	- ^c	2.0	- ^c	- ^c
Ta	27,000	0.2	0.1	-542	- ^c	2.0	- ^c	- ^c
<u>At 160°C</u>								
R60705	3,300	1.2	1.0	-728	- ^c	3.0	- ^c	- ^c
R60702	10,000	0.4	0.4	-872	- ^c	2.0	- ^c	- ^c
KBI-40	6,000	0.6	0.5	-589	- ^c	1.5	- ^c	- ^c
Ta	42,000	0.1	0.1	-450	- ^c	1.0	- ^c	- ^c
<u>At 170°C</u>								
R60705	1,540	2.5	2.0	-612	- ^c	3.0	- ^c	- ^c
R60702	5,200	0.8	0.7	-504	- ^c	2.0	- ^c	- ^c
KBI-40	4,300	0.9	0.6	-578	- ^c	2.0	- ^c	- ^c
Ta	30,000	0.1	0.1	-677	- ^c	1.0	- ^c	- ^c
<u>At 180°C</u>								
R60705	850	4.6	4.0	-805	- ^c	5.0	- ^c	- ^c
R60702	1,800	2.2	2.0	-781	- ^c	3.0	- ^c	- ^c
KBI-40	4,500	0.9	0.6	-765	- ^c	2.0	- ^c	- ^c
Ta	22,000	0.2	0.1	-641	- ^c	1.0	- ^c	- ^c
<u>At 190°C</u>								
R60705	810	4.8	5.0	-726	- ^c	15.0	- ^c	- ^c
R60702	1170	3.3	3.0	-570	- ^c	5.0	- ^c	- ^c
KBI-40	8500	0.7	0.3	-631	- ^c	3.0	- ^c	- ^c
Ta	46000	0.1	0.1	-542	- ^c	1.0	- ^c	- ^c
<u>At 200°C</u>								
R60705	750	5.2	7.0	-359	- ^c	30.0	- ^c	1,400
R60702	1,009	3.8	4.0	-345	- ^c	8.0	- ^c	1,400
KBI-40	2,100	1.9	1.0	-279	- ^c	5.0	- ^c	- ^c
Ta	35,000	0.1	0.1	-432	- ^c	2.0	- ^c	- ^c
<u>At 210°C</u>								
R60705	680	13.9	13.0	-376	- ^c	10.0	- ^c	1,400
R60702	1,000	5.7	6.0	-368	- ^c	8.0	- ^c	1,600
KBI-40	1,000	3.9	3.0	-368	- ^c	8.0	- ^c	1,600
Ta	7,500	0.5	0.4	-587	- ^c	3.0	- ^c	1,700
<u>At 220°C</u>								
R6005	190	20.4	20.0	-402	- ^c	00.0	- ^c	1,400
R6002	0	6.5	7.0	-343	- ^c	10.0	- ^c	1,250
KBI-40	1,600	2.4	2.0	-291	- ^c	10.0	- ^c	1,600
Ta	3,300	1.2	1.0	-247	- ^c	3.0	- ^c	- ^c

^a Less than 0.1 ^b: No passivation observed. ^c: Outside measured range of potential. ^d Can not determine.

was 1 to 1.5 $\mu\text{A}/\text{cm}^2$. Thus, no corrosion protection is needed for N08026 at temperatures near the boiling point. At 120°C, all four stainless steels corroded excessively. Corrosion rates of alloys S31603, N08904, and N08020 were 1000, 26, and 51 mpy, respectively, while alloy N08026 corroded at a rate of 10 mpy. Thus, alloys of this class are not satisfactory for hydrolysis service at 120°C. Although passivation was observed on these test alloys, the passive and critical current densities were high and the passivation range was narrow. Thus, anodic protection would be difficult and uneconomical under these conditions.

Nickel and Ni-Cu Alloy

Without addition of alloying elements, nickel N02200 (Nickel 200) only showed fair corrosion resistance (corrosion rate of 12 mpy) at 90°C and poor corrosion resistance (corrosion rate exceeding 200 mpy) at 100 and 120°C. Thus, metal N02200 is unsatisfactory for hydrolysis service at temperatures near or above 90°C.

Because of the high copper content, corrosion performance of alloy N04400 (Monel 400, 30% Cu-70% Ni) is better than commercial nickel in 5 wt% sulfuric acid. The alloy showed excellent resistance (corroded at rate of less than 2 mpy at 90°C). However, corrosion of alloy N04400 increased as temperature increased. Corrosion resistance of alloy N04400 shifted from excellent (2 mpy) at 90°C, to good (4 mpy) at 100°C, to fair (16 mpy) at 120°C, and to poor (674 mpy) at 140°C.

Potentiodynamic polarization test results indicate that neither alloy N02200 nor alloy N04400 showed passivity. Both anodic and cathodic polarizations of alloy N02200 and alloy N04400 exhibited classic Tafel behavior (Fig 1). At all test temperatures, an almost vertical-slope segment was observed on the cathodic polarization curves of alloy N04400, but no similar segment was seen on alloy N02200 (Fig 1 and 2). This behavior indicates that diffusion of cathodic species is a rate-controlling step in the corrosion of alloy N04400, but not in N02200. Transport of reactant species through

the thick film of corrosion products was attributed to diffusion. The increase in corrosion of alloys N02200 and N04400 corrosion with temperature was also evidenced by shifting of the alloy polarization curves in the direction of increased current density as the test temperatures was increased.

Ni-Mo Alloy

Only alloy N10665 (Hastelloy B-2, 28% Mo-69% Ni) is available as a commercial alloy in this class. Process experience indicated that alloy N10665 has excellent resistance to corrosion in reducing acids such as hydrochloric and dilute sulfuric acids at moderate temperatures (ASM 1985). The AC impedance test showed that alloy N10665 had excellent corrosion resistance to 5 wt% sulfuric acid at 90 and 100°C. Corrosion rates were 1 and 2 mpy, respectively. The corrosion rate increased significantly to 15 and 299 mpy when temperatures were increased to 120 and 140°C. Similar to test results on N02200 and N04400, alloy N10665 did not passivate in the 5 wt% sulfuric acid solution. The anodic polarization curves exhibited a classical Tafel relationship. An increase in alloy N10665 corrosion was evidenced by shifting of the alloy polarization curves in the direction of increased current density.

Ni-Cr-Mo-Fe Alloys

The two representative alloys of this class selected for testing were alloy N08825 (Incoloy 825, 22% Cr-29% Fe-3% Mo-42% Ni) and alloy N06030 (Hastelloy G-30, 30% Cr-15% Fe-5.5% Mo-43% Ni). With higher chromium and lower iron content, alloy N06030 is expected to corrode less severely than alloy N08825 in the 5 wt% sulfuric acid solution. At 90°C, both materials exhibited excellent resistance to corrosion. The corrosion rate was less than 1 mpy. Examination of anodic polarization curves showed stable passivation of alloys N06030 and N08825 and low passive current densities, 1.5 and 2.5 $\mu\text{A}/\text{cm}^2$, respectively (Fig 1). Both alloys passivated spontaneously and corroded in the passive range when tested at 90°C because the

corrosion potential was more noble than the primary passivation potential, E_{pp} . The E_{pp} was not found in the anodic polarization measurements for either alloy at 90°C because it was more active than the low end of the test range. The breakdown potential of both alloys was approximately 290 mV/Pt. Similar results were observed when these alloys were tested at 100°C. Both test materials showed excellent corrosion resistance with corrosion rates of less than 1 mpy. Stable passivation was also found in both test materials with low passive current densities, 3 $\mu\text{A}/\text{cm}^2$ for alloy N08825 and 1 $\mu\text{A}/\text{cm}^2$ for alloy N06030. Both alloys had a breakdown potential of 363 mV/Pt.

Corrosion increased significantly when the alloys were tested at 120°C. Both alloys N06030 and N08825 showed fair corrosion resistance with corrosion rates of 8 to 9 mpy. Although passivation was still observed on these alloys, it was less stable and protective because the passive current density was relatively high, 9 to 10 $\mu\text{A}/\text{cm}^2$ (Fig 2). The corrosion potential of alloy N08825 became more active than the E_{pp} . This indicated that corrosion of the alloy shifted completely to the active region. At 120°C, corrosion of alloy N06030 still remained in the passive range because the corrosion potential was more noble than E_{pp} . However, the corrosion rate was high because alloy N06030 passivated at a high passive current density (9 $\mu\text{A}/\text{cm}^2$). Moreover, the corrosion potential of alloy N06030 was only slightly more noble than the E_{pp} , approximately 45 mV. Thus, alloy N06030 could easily corrode in the active or active-passive region. General corrosion of both alloys N08825 and N06030 was high at 140°C. The rates were in the hundreds of mpy. Passivation of these two alloys was unstable and unprotective. The passive range was narrow and i_c was exceedingly high, approximately 50 $\mu\text{A}/\text{cm}^2$ for alloy N06030 and 100 $\mu\text{A}/\text{cm}^2$ for alloy N08825.

Ni-Cr-Mo Alloys

Alloys N08625 (Inconel 625, 22% Cr-5.0 Fe-9% Mo-4% Nb-62% Ni), N06022 (Hastelloy C-22, 22% Cr-10% Mo-2% Nb-3% W-53% Ni), and

N10276 (Hastelloy C-276, 16% Cr-5.5% Fe-16% Mo-4% W-57% Ni) were selected in this class of alloys. In the chemical process industry, these alloys have shown excellent corrosion resistance to various acid environments (ASM 1985). Similar to results of the Ni-Cr-Mo-Fe alloys, these test materials exhibited excellent corrosion resistance at temperatures approaching 100°C. The alloys corroded at rates less than 1 mpy. AC impedance analysis showed that corrosion resistance of these alloys shifted to fair and to unsatisfactory as test temperatures were increased to 120 and 140°C, respectively.

Potentiodynamic polarization tests showed that the Ni-Cr-Mo-W alloys passivated in the same manner as the Ni-Cr-Mo-Fe alloys in 5 wt% sulfuric acid. Passivation was stable and occurred spontaneously in 5 wt% sulfuric acid at 90 and 100°C (Fig 1). The passive current densities of these alloys were low, 1.5 to 2.5 $\mu\text{A}/\text{cm}^2$. As test temperature increased, passivation of these alloys shifted toward conditions favorable for higher corrosion rates. Passivation was neither stable nor protective at 120°C, because the values of i_{pp} and i_c were high. The i_c values of these alloys were approximately 4 to 5 times higher than those observed at 90 and 100°C. At 140°C, the i_p values of all three alloys were unacceptably high, 50 $\mu\text{A}/\text{cm}^2$ and higher. Therefore, anodic protection would not be feasible under these conditions.

Zirconium Alloys

Tests were conducted on two zirconium alloys R60705 (Grade Zr 705) and R60702 (Grade Zr 702). Alloy R60705 contains approximately 91 wt% zirconium (Zr), 4.5 wt% hafnium (Hf), and 3 wt% manganese (Mn). Zirconium 702 is purer and contains approximately 95 wt% Zr, 4.5 wt% Hf, and no Mn. Because of its purity, R60702 normally exhibits better corrosion resistance than R60705 in most corrosive environments. However, R60705 is slightly less expensive than R60702. Generally, zirconium alloys are excellent corrosion-resistant materials when exposed to reducing environments, particularly hydrochloric acid and sulfuric acid solutions (ASM 1985).

AC impedance tests revealed that both zirconium alloys showed excellent corrosion resistance to the 5 wt% sulfuric acid solution at temperatures up to 170°C. The corrosion rate was less than 1 mpy. Impedance of both alloy corrosion systems was extremely high, over several thousand ohms. At 180°C, alloy R60702 still showed excellent resistance to general corrosion in the 5 wt% sulfuric acid solution. The corrosion rate was approximately 2 mpy. Corrosion resistance of alloy R60702 was good (corrosion rate of 3 to 4 mpy) at 190 and 200°C and was fair at 210 and 220°C (corrosion rate of 5 and 6 mpy). Corrosion of alloy R60705 increased significantly at temperatures above 170°C. The alloy showed good corrosion resistance (4 mpy) at 180 and 190°C, fair resistance (7 mpy) at 200°C, and poor resistance at 210 and 220°C (13 and 20 mpy, respectively).

Potentiodynamic polarization tests revealed that passivation of zirconium alloys was stable and spontaneous over a wide range of applied potential (Fig 1-3). The corrosion potential of both alloys was more noble than E_{pp} at all test temperatures. Strong and protective passivation of the alloys was also demonstrated by the fact that E_{pp} and E_b values were completely beyond the test range and could not be determined at temperatures below 200°C (Fig. 3). In addition, passive current density was low at most test temperatures, less than 3 $\mu\text{A}/\text{cm}^2$. At test temperatures of 200°C and above, E_{pp} became visible on the anodic polarization curves; however, it was as high as 1400 mV/Pt. Passivation of alloy R60705 became less protective at between 190° to 220°C. The passive current density was between 5 and 7 $\mu\text{A}/\text{cm}^2$ at 190 and 200°C and between 6 and 20 $\mu\text{A}/\text{cm}^2$ at 210 and 220°C. Although corrosion of alloy R60705 increased significantly with test temperatures, particularly above 180°C, the passivation of the alloy was still spontaneous. Corrosion still occurred in the passive range. No active or active-passive corrosion region was found on the anodic polarization of alloy R60705 for the temperatures tested.

Similar to alloy R60705, stable passivation occurred for alloy R60702 at all test

temperatures (Fig 1-3). The passive current density was as low as 1 $\mu\text{A}/\text{cm}^2$ at temperatures below 180°C. At test temperatures 180°C and above, the passivation of alloy R60702 shifted in the direction of increasing corrosion. The passive current density increased from 2 to 3 $\mu\text{A}/\text{cm}^2$ as temperature was increased from 170 to 180°C and then increased to 5, 8, 10, and 10 $\mu\text{A}/\text{cm}^2$ as temperature was increased to 190, 200, 210, and 220°C, respectively. The corrosion resistance of alloy R60702 was better than that of alloy R60705 at all test temperatures.

Tantalum and Nb-Ta Alloys

Tantalum and tantalum alloys are considered the best corrosion-resistant materials for exposure to both oxidizing and reducing mineral acids over wide ranges of concentration and temperature (ASM 1985). However, high costs have limited their use. Tantalum has been used only in severe conditions for which there were no suitable alternative metals. Among the commercial Ta alloys, KBI-40, an alloy containing 60% Ta and 40% Nb, is considered a superior corrosion-resistant material for many environments. AC impedance measurements showed that Ta has excellent corrosion resistance to 5 wt% sulfuric acid at temperatures up to 220°C. The polarization resistance extrapolated from AC impedance data is many thousands ohms. Tantalum exhibited complete stability and spontaneous passivation without evidence of breakdown over a wide range of potentials. Except at 210 and 220°C, the passive range was so large that neither primary nor breakdown potentials of tantalum were observed on the anodic polarization curves. The corrosion potential of tantalum was more noble than E_{pp} , so tantalum corroded in the passive range at all test temperatures. Temperature had negligible effect on the passive current density of tantalum up to 190°C. The passive current density was 1 $\mu\text{A}/\text{cm}^2$ or less. At 200, 210, and 220°C, i_p increased slightly to approximately 3 $\mu\text{A}/\text{cm}^2$; however, the metal remained in stable and spontaneous passivation.

AC impedance tests for KBI-40 also showed excellent corrosion resistance in the 5 wt%

sulfuric acid solution up to 200°C with a corrosion rate of less than 1 mpy. The corrosion rate was 3 and 2 mpy at 210 and 220°C, respectively. Potentiodynamic polarization tests showed that passivation of KBI-40 was spontaneous up to 200°C. At higher test temperatures, although spontaneous passivation was still observed, the anodic polarization curves of KBI-40 shifted toward increasing the passive current density. The passive current density shifted from 2 to 5 $\mu\text{A}/\text{cm}^2$ when the test temperature was increased from 190 to 200°C. At 210 and 220°C, the passivation of KBI-40 was less protective, because the passive current density increased to 8 and 10 $\mu\text{A}/\text{cm}^2$, respectively.

Conclusions

Stainless Steels

At 90 and 100°C, strong evidence of stable passivation was observed on stainless steels S31603, N08904, and N08020; however, resistance to general corrosion was fair to poor when exposed to 5 wt% sulfuric acid. If these alloys are selected, additional corrosion protection is advised to protect these stainless steels from excessive corrosion. Alloy N08026 showed excellent corrosion resistance to 5 wt% sulfuric acid at temperatures to 100°C. The alloy exhibited stable and spontaneous passivation. At 120°C and above, all stainless steels exhibited unstable and unprotective passivation. These alloys are unsatisfactory for service with the dilute sulfuric acid in this temperature range.

Nickel, Ni-Cu and Ni-Mo Alloys

Alloy N02200 exhibited unsatisfactory corrosion resistance due to high corrosion rates in 5 wt% sulfuric acid at temperatures of 90°C and above. Alloy N02200 did not passivate under any test conditions. Alloy N04400 exhibited excellent corrosion resistance at 90°C and good corrosion resistance at 100°C. At temperatures above 100°C, the alloy corroded severely. Alloy N10665 showed excellent corrosion resistance to

5 wt% sulfuric acid at temperatures up to 100°C. However, corrosion resistance of alloy N10665 is inadequate in 5 wt% sulfuric acid at temperatures of 120°C and above. The alloy corroded at excessive rates. Similar to the behavior of alloy N02200, no passivation was observed on alloys N04400 and N10665 in 5 wt% sulfuric acid at any test temperature.

Ni-Cr-Mo-Fe and Ni-Cr-Mo-W

These alloys showed excellent corrosion resistance in 5 wt% sulfuric acid at temperatures up to 100°C. All test alloys corroded at rates of less than 2 mpy. At 120°C, these alloys corroded at rates exceeding 5 mpy. At temperatures of 140°C and higher, these alloys are unsatisfactory for service with the dilute sulfuric acid. These alloys showed stable and spontaneous passivation at temperatures to 100°C. At 120°C and above, the passivation was unstable and unprotective. Because of high critical and passive current densities, application of anodic protection is not recommended for these nickel-based alloys at temperatures of 120°C or above.

Zirconium Alloys

Zirconium alloys R60705 and R60702 showed excellent corrosion resistance in 5 wt% sulfuric acid up to 170 and 180°C, respectively. Zirconium alloy R60705 has good corrosion resistance at temperatures of 180° and 190°C; however, the corrosion resistance of R60705 declined to fair at temperature of 200°C and above. Zirconium alloy R60702 showed good corrosion resistance at temperatures of 190 and 200°C, but only fair corrosion resistance at 210 and 220°C. R60705 showed stable and spontaneously passivation up to 170°C. The passivation was less protective at 180°C and above. Alloy R60702 exhibited stable and spontaneous passivation up to 190°C. At temperatures of 200°C and above, passivation was less protective.

Tantalum and Nb-Ta Alloys

Tantalum had excellent corrosion resistance at all test temperatures. The corrosion rate of Ta did

not exceed 0.1 mpy at test temperatures up to 200°C and approximately 1 mpy at 210 and 220°C. Tantalum also passivated stably and spontaneously at all test temperatures. The KBI-40 (40% Nb-60%Ta alloy) showed results similar to those obtained on tantalum. The alloy corroded at rates of 1 mpy or less at temperatures up to 200°C. KBI-40 showed good-to-excellent corrosion resistance at 210 and 220°C. The alloy passivated stably and spontaneously up to 200°C. At temperatures of 210 and 220°C, stable passivation was still observed, but there was less protection due to passive current density's being somewhat high (5-10 $\mu\text{A}/\text{cm}^2$).

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Figure 1. Potentiodynamic polarization of test metals at 90°C

Figure 2. Potentiodynamic polarization of test metals at 120°C

Figure 3. Potentiodynamic polarization of test metals at 140°C

Figure 4. Potentiodynamic polarization of refractory metals at various temperatures

Figure 5. AC impedance Nyquist plots of test metals at various temperatures

Figure 1 - Potentiodynamic polarization of Test Materials Exposed to 5 wt% Sulfuric Acid at 90°C Under Static Conditions. Test at Scan Rate of 0.17 mV/s.

Figure 2 - Potentiodynamic polarization of Test Materials Exposed to 5 wt% Sulfuric Acid at 120°C Under Static Conditions. Test at Scan Rate of 0.17 mV/s.

Figure 3 - Potentiodynamic polarization of Test Materials Exposed to 5 wt% Sulfuric Acid at 140 °C Under Static Conditions. Test at Scan Rate of 0.17 mV/s.

Figure 4 - Potentiodynamic polarization of Refractory Metals Exposed to 5 wt% Sulfuric Acid at Various Temperatures Under Static Conditions. Test at Scan rate of 0.17 mV/s.

Figure 5 - AC Impedance Nyquist Plots of Test Materials in 5 wt% sulfuric Acid at Various Temperatures