

APPENDIX O
CRITICAL AND CORROSION POTENTIALS FOR ALLOY 22
(RESPONSE TO CLST 1.10 AND CLST 1.11)

Note Regarding the Status of Supporting Technical Information

This document was prepared using the most current information available at the time of its development. This Technical Basis Document and its appendices providing Key Technical Issue Agreement responses that were prepared using preliminary or draft information reflect the status of the Yucca Mountain Project's scientific and design bases at the time of submittal. In some cases this involved the use of draft Analysis and Model Reports (AMRs) and other draft references whose contents may change with time. Information that evolves through subsequent revisions of the AMRs and other references will be reflected in the License Application (LA) as the approved analyses of record at the time of LA submittal. Consequently, the Project will not routinely update either this Technical Basis Document or its Key Technical Issue Agreement appendices to reflect changes in the supporting references prior to submittal of the LA.

APPENDIX O

CRITICAL AND CORROSION POTENTIALS FOR ALLOY 22 (RESPONSE TO CLST 1.10 AND CLST 1.11)

This appendix provides a response to Key Technical Issue (KTI) agreements Container Life and Source Term (CLST) 1.10 and CLST 1.11. These KTI agreements are related to the influence of different variables, such as temperature, electrolyte composition, and metallurgical conditions of the alloys, on the corrosion potential and critical potentials for localized corrosion.

O.1 KEY TECHNICAL ISSUE AGREEMENTS

O.1.1 CLST 1.10 and CLST 1.11

Agreement CLST 1.10 and CLST 1.11 were reached during the U.S. Nuclear Regulatory Commission (NRC)/U.S. Department of Energy (DOE) technical exchange and management meeting on CLST held September 12 to 13, 2000, in Las Vegas, Nevada. Subissues 1, 2, 3, 4, and 6 were discussed at the meeting (Schlueter 2000).

Wording of the agreements is as follows:

CLST 1.10¹

Provide the documentation for Alloy 22 and titanium for the path forward items listed on slide 21 and 22. DOE will provide the documentation in a revision to AMRs (ANL-EBS-MD-000003 and ANL-EBS-MD-000004) prior to LA.

CLST 1.11

Provide the technical basis for the selection of the critical potentials as bounding parameters for localized corrosion, taking into account MIC. DOE will provide the documentation in a revision to the AMRs (ANL-EBS-MD-000003 and ANL-EBS-MD-000004) prior to LA.

O.1.2 Related Key Technical Issues

Related KTI agreements include CLST 1.01, CLST 1.02 (Appendix I), CLST 1.08 (Appendix N), and CLST 6.01 (Appendix P).

¹ The path forward items in slides 21 and 22 are as follows: (1) measure corrosion potentials on the Long Term Corrosion Test Facility (LTCTF) to determine any shift of the potential with time toward the critical potentials for localized corrosion; (2) determine critical potentials on welded and aged coupons of Alloy 22 (UNS N06022) versus those for base metal, which is particularly important if precipitation of severe segregation of alloying elements occurs in the welds; (3) separate effects of ionic mix of species in Yucca Mountain waters on critical potential-damaging species (chloride, fluoride, possibly sulfate) from the potentially beneficial species (nitrate, carbonate, silicate) because pore water, perched water, and groundwater have somewhat different ionic ratios; and (4) determine critical potentials in environments containing heavy metal concentrations (e.g., lead, arsenic, and mercury).

There has been no submittal related to these KTI agreements to the NRC.

CLST 1.10 and CLST 1.11 are related to the characterization of localized corrosion that may nucleate and grow on the corrosion-resistant layer of the waste package and the drip shield under normal repository operating conditions. The current degradation model includes localized corrosion if the free corrosion potential (E_{corr}) is equal to or higher than the critical potential for localized corrosion (E_{crit}) (BSC 2003a; BSC 2003b).

O.2 RELEVANCE TO REPOSITORY PERFORMANCE

The model for the prediction of the lifetime of the waste package in Yucca Mountain includes three modes of degradation. Two of these modes are general corrosion and localized corrosion (crevice corrosion). The occurrence of these modes of corrosion depends not only on the electrolyte composition and temperature of the environment in contact with the waste package but also on the E_{corr} of the metal surface. The conditions that cause localized corrosion in Alloy 22 and Titanium Grade 7 (R52400) determine the lifetime of both the waste package outer shell and the drip shield. The third degradation mode is stress corrosion cracking, which is discussed in Section 9 of this technical basis document.

The values of E_{corr} and E_{crit} that are associated with Alloy 22 and Titanium Grade 7 in a series of electrolyte solutions determine the margin of safety against localized corrosion. If E_{crit} less E_{corr} (ΔE) is greater than 0, only passive corrosion is expected to occur. The larger the value of ΔE , the larger the margin of safety against the onset of localized corrosion. The values of E_{corr} and E_{crit} are measured independently of each other. The values of E_{corr} and E_{crit} depend on metallurgical variables, as well as on environmental variables, such as the electrolyte composition and the temperature. Together with the temperature, the electrolyte composition is one of the most important factors that may control the performance of the container regarding localized corrosion. It is important to characterize the opposing roles of aggressive species, such as chloride, and beneficial species, such as nitrate, to determine in which region of composition the alloys are expected to undergo localized corrosion (crevice corrosion).

This response addresses issues related to the performance of Alloy 22. The performance of Titanium Grade 7 is addressed in the response to CLST 6.01 (Appendix P).

O.3 RESPONSE

The localized corrosion susceptibility of Alloy 22 is explained using two parameters or properties of the alloy: E_{corr} and E_{crit} . E_{corr} is the potential that a metal adopts when it is immersed in an electrolyte solution. E_{crit} is a potential above which the metal suffers localized corrosion. If ΔE is greater than 0, the alloy is expected to undergo slow passive dissolution. However, if ΔE is 0 or less, it is possible that localized corrosion (mainly crevice corrosion) may develop if tight, occluded regions (crevices) are present on the surface of the alloy. The values of E_{corr} and E_{crit} are dependent on environmental variables, such as electrolyte composition, pH, temperature, and redox potential.

The values of E_{corr} and E_{crit} that Alloy 22 adopts when environmental and metallurgical variables, such as temperature, chloride concentration, presence of nitrate, weld seams, and thermally aged microstructures, are changed are summarized as follows:

- ΔE is positive for the behavior of Alloy 22 in simulated concentrated groundwater, such as simulated acidified water (SAW) and simulated concentrated water (SCW). Crevice corrosion was not observed in these solutions, even at temperatures near the boiling point.
- For pure 5 mol/L CaCl_2 brine at 120°C, Alloy 22 suffers both pitting and crevice corrosion at the E_{corr} in aerated conditions. These consequences are predicted by the value of ΔE and are shown experimentally using potentiostatic tests and immersion tests at the free corrosion potential.
- Nitrate is a strong crevice corrosion inhibitor. The addition of nitrate to pure chloride brines increases the E_{crit} of Alloy 22.
- Sulfate is an inhibitor for crevice corrosion but to a lesser degree than nitrate. Silicate is also an inhibitor, but to a lesser degree than sulfate. Alloy 22 is not susceptible to crevice corrosion in SCW solution, which contains nitrate, sulfate, carbonate, and silicate ions.
- Fluoride ions in pure form do not affect the resistance of Alloy 22 to localized corrosion. However, fluoride may cause chloride to become more aggressive for localized corrosion.
- Current studies in aggressive solutions show that welded Alloy 22 is not more susceptible to localized corrosion than the base wrought metal. Thermally aged material did not show an increased susceptibility to localized corrosion.
- The effect of heavy metals and microbially influenced corrosion (MIC) is small compared to other variables, such as chloride and temperature.

The information in this report is responsive to agreements CLST 1.10 and CLST 1.11 made between the DOE and NRC. The report contains the information that DOE considers necessary for NRC review for closure of these agreements.

O.4 BASIS FOR THE RESPONSE

O.4.1 Corrosion Potential of Alloy 22

When a metallic component is immersed in an electrolyte, it adopts a characteristic potential called the corrosion potential (E_{corr}). The value of E_{corr} depends on the type of electrolyte solution, temperature, the type of alloy, and its surface characteristics. The first item of CLST 1.10 specified that the E_{corr} of Alloy 22 was going to be measured in the Long Term Corrosion Test Facility (LTCTF). To avoid disturbing the testing conditions of the other specimens housed in the LTCTF vessels, representative specimens, along with approximately

2 L of the initial solutions, were removed from the large vessels and transported to bench-top experiments. These were the initial six bench-top cells containing SAW, SCW, and simulated dilute water (SDW) at 60°C and 90°C. Later, these cells were expanded to include more than 30 different conditions of electrolyte composition, temperature, and metallurgical compositions. The electrolyte solutions include multi-ionic solutions simulating concentrated groundwater, such as SAW, SCW, SDW, and basic saturated water (BSW), as well as simpler solutions, such as oxalic acid, sodium fluoride, and several variations of chloride and nitrate brines. Testing temperatures range from ambient to 120°C. Metallurgical compositions of the specimens include: (1) mill-annealed rods and multiple crevice assemblies, (2) as-welded rods and multiple crevice assemblies, (3) welded plus aged rods, and (4) welded, welded plus aged, and black-annealed prism crevice assemblies. Tables O-1 and O-2 list some of the E_{corr} values for Alloy 22, which were measured in aerated conditions for times of 1 year or longer. The E_{corr} data in Tables O-1 and O-2 and Figure O-1 are qualitative for comparative or illustrative purposes only. These are not actual average values but trends that describe the E_{corr} as low (active state or negative; e.g., -200 mV) or high (passive state of positive; e.g., +400 mV). The project has a larger set of data on E_{corr} contained in DTNs: LL040402212251.084 and LL040402112251.083. DTN: LL040402112251.083 contains the evolution of each individual exposed electrode as a function of time for more than 100 electrodes for times as long as 3 years. This larger set of E_{corr} data at various environments and temperatures is shown in Table O-3.

Table O-1. Ranges of Corrosion Potential for Alloy 22 and Platinum in Simulated Concentrated Groundwaters

Cell / Electrolyte	Pt Rod (mV)	Mill-Annealed U-bend (mV)	Mill-Annealed Rod (mV)	As-Welded Rod (mV)
2 / SAW, 90°C	380	380	NA	NA
9 / SAW, 90°C	400	NA	390	NA
10 / SAW, 90°C	380	NA	380	NA
1 / SAW, 60°C	420	400	NA	NA
7N / SAW, Ambient	350	NA	240	NA
16 / SCW, 90°C	200	NA	-200	-210
3 / SCW, 90°C	60	-50	NA	NA
6 / SDW, 90°C	140	90	NA	NA
4 / BSW, 105°C	90	20	NA	NA
19 / BSW, 105°C	20	NA	-200	-240

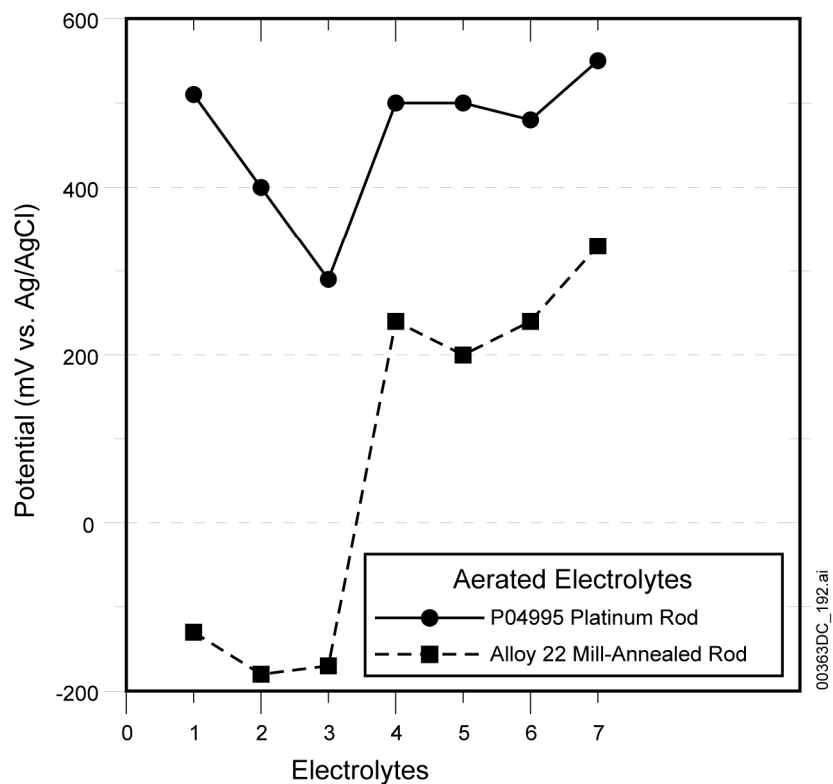
Source: DTNs: LL040402212251.084, LL040402112251.083.

Table O-2. Ranges of Corrosion Potentials for Alloy 22 in Simpler Electrolytes

Cell	Electrolyte	Pt Rod (mV)	Mill-Annealed Rod (mV)	As-Welded Rod (mV)	Welded Plus Aged Rod (mV)	Mill-Annealed Multiple Crevice Assembly (mV)	As-Welded Multiple Crevice Assembly (mV)
8	5 mol/L CaCl_2 , 120°C	510	-130	NA	NA	NA	NA
18	4 mol/L NaCl, 90°C	290	-160	-100	120	NA	NA
20	5 mol/L CaCl_2 , 120°C	400	-200	-70	290	-100	-100
14	5 mol/L CaCl_2 + 0.05 mol/L $\text{Ca}(\text{NO}_3)_2$, 90°C	500	270	170	400, 80	NA	NA
15	5 mol/L CaCl_2 + 0.5 mol/L $\text{Ca}(\text{NO}_3)_2$, 90°C	500	200	230	250	NA	NA
21	5 mol/L CaCl_2 + 0.5 mol/L $\text{Ca}(\text{NO}_3)_2$, 90°C	480	280	470	470	10	240
13	1 mol/L CaCl_2 + 1 mol/L $\text{Ca}(\text{NO}_3)_2$, 90°C	550	350	360	520	NA	NA

Source: DTNs: LL040402212251.084, LL040402112251.083.

NOTE: Welded plus aged rods were heat treated for 173 hours at 700°C.



- (1) 5 mol/L CaCl_2 , 120°C
 (2) 5 mol/L CaCl_2 , 120°C
 (3) 4 mol/L NaCl , 90°C
 (4) 5 mol/L CaCl_2 + 0.05 mol/L $\text{Ca}(\text{NO}_3)_2$, 90°C
 (5) 5 mol/L CaCl_2 + 0.5 mol/L $\text{Ca}(\text{NO}_3)_2$, 90°C
 (6) 5 mol/L CaCl_2 + 0.5 mol/L $\text{Ca}(\text{NO}_3)_2$, 90°C
 (7) 1 mol/L CaCl_2 + 1 mol/L $\text{Ca}(\text{NO}_3)_2$, 90°C

Source: DTN: LL040402212251.084.

Figure O-1. E_{corr} of Alloy 22 and Platinum in Chloride and Chloride plus Nitrate Brines

Table O-3. Long-Term Corrosion Potential Measurements

Cell No.	Sample ID	Sample Type	Solution	pH Before	pH After	Calculated Composition		Measured Composition		Temp (°C)	E_{corr} (mV vs. Ag/AgCl)
						Cl (mol/kg)	NO ₃ (mol/kg)	Cl (mol/kg)	NO ₃ (mol/kg)		
8	DEA 105	MA Alloy 22 Rod	5 mol/L CaCl ₂	5.21	4.92	12.0		ND	0.00186	120	-126
8	DEA 106	MA Alloy 22 Rod	5 mol/L CaCl ₂	5.21	4.92	12.0		ND	0.00186	120	-139
8	DEA 107	MA Alloy 22 Rod	5 mol/L CaCl ₂	5.21	4.92	12.0		ND	0.00186	120	-150
8	DEA 108	MA Alloy 22 Rod	5 mol/L CaCl ₂	5.21	4.92	12.0		ND	0.00186	120	-126
8	DEA 109	MA Alloy 22Rod	5 mol/L CaCl ₂	5.21	4.92	12.0		ND	0.00186	120	-133
20	DEA 2824	MA Alloy 22 Rod	5 mol/L CaCl ₂	5.9	N/A	12.0				120	-159
20	DEA 2825	MA Alloy 22 Rod	5 mol/L CaCl ₂	5.9	N/A	12.0				120	-107
20	DEA 2826	MA Alloy 22Rod	5 mol/L CaCl ₂	5.9	N/A	12.0				120	-93.3
20	JE2052	ASW Alloy 22 Rod	5 mol/L CaCl ₂	5.9	N/A	12.0				120	-2.55
20	JE2053	ASW Alloy 22 Rod	5 mol/L CaCl ₂	5.9	N/A	12.0				120	11.7
20	JE2054	ASW Alloy 22 Rod	5 mol/L CaCl ₂	5.9	N/A	12.0				120	55.1
20	JE2024	WPA Alloy 22 Rod	5 mol/L CaCl ₂	5.9	N/A	12.0				120	257
18	DEA 2816	MA Alloy 22Rod	4 mol/L NaCl	6.86	6.3					90	-168
18	DEA 2817	MA Alloy 22Rod	4 mol/L NaCl	6.86	6.3					90	-161
18	DEA 2818	MA Alloy 22 Rod	4 mol/L NaCl	6.86	6.3					90	-167
18	JE 2045	ASW Alloy 22 Rod	4 mol/L NaCl	6.86	6.3					90	-122
18	JE 2046	ASW Alloy 22 Rod	4 mol/L NaCl	6.86	6.3					90	-78.4
18	JE 2047	ASW Alloy 22 Rod	4 mol/L NaCl	6.86	6.3					90	-80.2
18	JE 2017	WPA Alloy 22 Rod	4 mol/L NaCl	6.86	6.3					90	185
18	JE 2018	WPA Alloy 22 Rod	4 mol/L NaCl	6.86	6.3					90	64.6
18	JE 2019	WPA Alloy 22 Rod	4 mol/L NaCl	6.86	6.3					90	94.9
14	DEA 2800	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.05 mol/L Ca(NO ₃) ₂	5.04	4.37	11.7	0.1186	21.6	0.197	90	148
14	DEA 2801	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.05 mol/L Ca(NO ₃) ₂	5.04	4.37	11.7	0.1186	21.6	0.197	90	278
14	DEA 2803	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.05 mol/L Ca(NO ₃) ₂	5.04	4.37	11.7	0.1186	21.6	0.197	90	56.7
14	DEA 2804	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.05 mol/L Ca(NO ₃) ₂	5.04	4.37	11.7	0.1186	21.6	0.197	90	104
14	JE 2035	ASW Alloy 22 Rod	5 mol/L CaCl ₂ + 0.05 mol/L Ca(NO ₃) ₂	5.04	4.37	11.7	0.1186	21.6	0.197	90	161
14	JE 2036	ASW Alloy 22 Rod	5 mol/L CaCl ₂ + 0.05 mol/L Ca(NO ₃) ₂	5.04	4.37	11.7	0.1186	21.6	0.197	90	205
14	JE 2007	WPA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.05 mol/L Ca(NO ₃) ₂	5.04	4.37	11.7	0.1186	21.6	0.197	90	439
14	JE 2008	WPA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.05 mol/L Ca(NO ₃) ₂	5.04	4.37	11.7	0.1186	21.6	0.197	90	-138
15	DEA 2805	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	4.19	4.98	12.6	1.2643	16.3	1.56	90	238
15	DEA 2806	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	4.19	4.98	12.6	1.2643	16.3	1.56	90	190
15	DEA 2808	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	4.19	4.98	12.6	1.2643	16.3	1.56	90	99.2

Table O-3. Long-Term Corrosion Potential Measurements (Continued)

Cell No.	Sample ID	Sample Type	Solution	pH Before	pH After	Calculated Composition		Measured Composition		Temp (°C)	E_{corr} (mV vs. Ag/AgCl)
						Cl (mol/kg)	NO ₃ (mol/kg)	Cl (mol/kg)	NO ₃ (mol/kg)		
15	DEA 2809	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	4.19	4.98	12.6	1.2643	16.3	1.56	90	89
15	JE 2037	ASW Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	4.19	4.98	12.6	1.2643	16.3	1.56	90	229
15	JE 2038	ASW Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	4.19	4.98	12.6	1.2643	16.3	1.56	90	282
15	JE 2009	WPA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	4.19	4.98	12.6	1.2643	16.3	1.56	90	230
15	JE 2010	WPA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	4.19	4.98	12.6	1.2643	16.3	1.56	90	290
21	DEA 2827	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	5.9	N/A	12.6	1.2643			90	405
21	DEA 2828	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	5.9	N/A	12.6	1.2643			90	390
21	DEA 2829	MA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	5.9	N/A	12.6	1.2643			90	-20.4
21	JE 2055	ASW Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	5.9	N/A	12.6	1.2643			90	486
21	JE 2056	ASW Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	5.9	N/A	12.6	1.2643			90	486
21	JE 2063	ASW Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	5.9	N/A	12.6	1.2643			90	487
21	JE 2025	WPA Alloy 22 Rod	5 mol/L CaCl ₂ + 0.5 mol/L Ca(NO ₃) ₂	5.9	N/A	12.6	1.2643			90	486
13	DEA 3087	MA Alloy 22 Rod	1 mol/L CaCl ₂ + 1 mol/L Ca(NO ₃) ₂	4.75	3.6			2.62	2.58	90	328
13	DEA 3088	MA Alloy 22 Rod	1 mol/L CaCl ₂ + 1 mol/L Ca(NO ₃) ₂	4.75	3.6			2.62	2.58	90	334
13	DEA 3089	MA Alloy 22 Rod	1 mol/L CaCl ₂ + 1 mol/L Ca(NO ₃) ₂	4.75	3.6			2.62	2.58	90	332
13	DEA 3090	MA Alloy 22 Rod	1 mol/L CaCl ₂ + 1 mol/L Ca(NO ₃) ₂	4.75	3.6			2.62	2.58	90	324
13	JE 2033	ASW Alloy 22 Rod	1 mol/L CaCl ₂ + 1 mol/L Ca(NO ₃) ₂	4.75	3.6			2.62	2.58	90	363
13	JE 2034	ASW Alloy 22 Rod	1 mol/L CaCl ₂ + 1 mol/L Ca(NO ₃) ₂	4.75	3.6			2.62	2.58	90	347
13	JE 2005	WPA Alloy 22 Rod	1 mol/L CaCl ₂ + 1 mol/L Ca(NO ₃) ₂	4.75	3.6			2.62	2.58	90	523
13	JE 2006	WPA Alloy 22 Rod	1 mol/L CaCl ₂ + 1 mol/L Ca(NO ₃) ₂	4.75	3.6			2.62	2.58	90	508
27	KE0 141	ASW Alloy 22 PCA	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	7.61	N/A	1	0.05			100	-167
27	KE0 142	ASW Alloy 22 PCA	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	7.61	N/A	1	0.05			100	-156
27	KE0 143	ASW Alloy 22 PCA	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	7.61	N/A	1	0.05			100	-160
27	KE0 144	ASW Alloy 22 PCA	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	7.61	N/A	1	0.05			100	-178
27	KE0 206	ASW + SHT Alloy 22 PCA	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	7.61	N/A	1	0.05			100	-66.5
27	KE0 207	ASW + SHT Alloy 22 PCA	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	7.61	N/A	1	0.05			100	-30.5
27	KE0 208	ASW + SHT Alloy 22 PCA	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	7.61	N/A	1	0.05			100	-25.4
27	KE0 209	ASW + SHT Alloy 22 PCA	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	7.61	N/A	1	0.05			100	-38.7
26	KE0 137	ASW Alloy 22 PCA	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	6.23	N/A	1	0.15			100	-185
26	KE0 138	ASW Alloy 22 PCA	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	6.23	N/A	1	0.15			100	-177
26	KE0 139	ASW Alloy 22 PCA	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	6.23	N/A	1	0.15			100	-170
26	KE0 140	ASW Alloy 22 PCA	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	6.23	N/A	1	0.15			100	-193
26	KE0 202	ASW + SHT Alloy 22 PCA	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	6.23	N/A	1	0.15			100	-44.3

Table O-3. Long-Term Corrosion Potential Measurements (Continued)

Cell No.	Sample ID	Sample Type	Solution	pH Before	pH After	Calculated Composition		Measured Composition		Temp (°C)	E_{corr} (mV vs. Ag/AgCl)
						Cl (mol/kg)	NO ₃ (mol/kg)	Cl (mol/kg)	NO ₃ (mol/kg)		
26	KE0 203	ASW + SHT Alloy 22 PCA	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	6.23	N/A	1	0.15			100	-42.5
26	KE0 204	ASW + SHT Alloy 22 PCA	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	6.23	N/A	1	0.15			100	-49.4
26	KE0 205	ASW + SHT Alloy 22 PCA	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	6.23	N/A	1	0.15			100	-45.9
25	KE0 133	ASW Alloy 22 PCA	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	7	N/A	3.5	0.175			100	-151
25	KE0 134	ASW Alloy 22 PCA	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	7	N/A	3.5	0.175			100	-165
25	KE0 135	ASW Alloy 22 PCA	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	7	N/A	3.5	0.175			100	-160
25	KE0 136	ASW Alloy 22 PCA	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	7	N/A	3.5	0.175			100	-167
24	KE0 129	ASW Alloy 22 PCA	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	6.67	N/A	3.5	0.525			100	-180
24	KE0 130	ASW Alloy 22 PCA	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	6.67	N/A	3.5	0.525			100	-175
24	KE0 131	ASW Alloy 22 PCA	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	6.67	N/A	3.5	0.525			100	-177
24	KE0 132	ASW Alloy 22 PCA	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	6.67	N/A	3.5	0.525			100	-181
24	KE0 194	ASW + SHT Alloy 22 PCA	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	6.67	N/A	3.5	0.525			100	-57.3
24	KE0 195	ASW + SHT Alloy 22 PCA	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	6.67	N/A	3.5	0.525			100	-28.7
24	KE0 196	ASW + SHT Alloy 22 PCA	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	6.67	N/A	3.5	0.525			100	-24.7
24	KE0 197	ASW + SHT Alloy 22 PCA	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	6.67	N/A	3.5	0.525			100	-27.2
22	KE0 121	ASW Alloy 22 PCA	6 mol/kg NaCl + 0.3 mol/kg KNO ₃	6.67	N/A	6	0.3			100	-135
22	KE0 122	ASW Alloy 22 PCA	6 mol/kg NaCl + 0.3 mol/kg KNO ₃	6.67	N/A	6	0.3			100	-144
22	KE0 123	ASW Alloy 22 PCA	6 mol/kg NaCl + 0.3 mol/kg KNO ₃	6.67	N/A	6	0.3			100	-131
22	KE0 124	ASW Alloy 22 PCA	6 mol/kg NaCl + 0.3 mol/kg KNO ₃	6.67	N/A	6	0.3			100	-134
23	KE0 125	ASW Alloy 22 PCA	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	6.31	N/A	6	0.9			100	-120
23	KE0 126	ASW Alloy 22 PCA	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	6.31	N/A	6	0.9			100	-116
23	KE0 127	ASW Alloy 22 PCA	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	6.31	N/A	6	0.9			100	-109
23	KE0 128	ASW Alloy 22 PCA	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	6.31	N/A	6	0.9			100	-129
23	KE0 190	ASW + SHT Alloy 22 PCA	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	6.31	N/A	6	0.9			100	6.33
23	KE0 191	ASW + SHT Alloy 222 PCA	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	6.31	N/A	6	0.9			100	27.8
23	KE0 192	ASW + SHT Alloy 22 PCA	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	6.31	N/A	6	0.9			100	23.8
23	KE0 193	ASW + SHT Alloy 22 PCA	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	6.31	N/A	6	0.9			100	32.9
4	ARC 22 U20A & ARC 22 U20B	MA Double U-Bend	BSW	11.05	8.77			4.38	2.63	105	66.7
4	DUB 163	Untested Weld U-Bend	BSW	11.05	8.77			4.38	2.63	105	13
19	DEA 2822	MA Alloy 22 Rod	BSW	12.87	10.49					105	-212
19	DEA 2823	MA Alloy 22 Rod	BSW	12.87	10.49					105	-194
19	JE 2050	ASW Alloy 22 Rod	BSW	12.87	10.49					105	-222

Table O-3. Long-Term Corrosion Potential Measurements (Continued)

Cell No.	Sample ID	Sample Type	Solution	pH Before	pH After	Calculated Composition		Measured Composition		Temp (°C)	E_{corr} (mV vs. Ag/AgCl)
						Cl (mol/kg)	NO ₃ (mol/kg)	Cl (mol/kg)	NO ₃ (mol/kg)		
19	JE 2051	ASW Alloy 22 Rod	BSW	12.87	10.49					105	-209
3	DUB 112	LTCTF welded U-Bend	Aged LTCTF SCW	10.72	10.91			0.214	0.114	90	-32
3	DUB 161	Untested welded U-Bend	Aged LTCTF SCW	10.72	10.91			0.214	0.114	90	-55
16	DEA 2810	MA Alloy 22 Rod	Fresh SCW	8.11	10.94					90	-221
16	DEA 2811	MA Alloy 22 Rod	Fresh SCW	8.11	10.94					90	-198
16	DEA 2812	MA Alloy 22 Rod	Fresh SCW	8.11	10.94					90	-175
16	JE 2039	ASW Alloy 22 Rod	Fresh SCW	8.11	10.94					90	-177
16	JE 2040	ASW Alloy 22 Rod	Fresh SCW	8.11	10.94					90	-174
16	JE 2041	ASW Alloy 22 Rod	Fresh SCW	8.11	10.94					90	-168
16	JE 2011	WPA Alloy 22 Rod	Fresh SCW	8.11	10.94					90	-4
16	JE 2012	WPA Alloy 22 Rod	Fresh SCW	8.11	10.94					90	84
16	JE 2013	WPA Alloy 22 Rod	Fresh SCW	8.11	10.94					90	34
6	DUB 132	LTCTF Welded U-Bend	Aged LTCTF SDW	8.55	8.5			0.00325	0.000313	90	81.3
6	DUB 162	Untested Welded U-Bend	Aged LTCTF SDW	8.55	8.5			0.00325	0.000313	90	108
2	DUB 052	LTCTF Welded U-Bend	Aged LTCTF SAW	3.55	4.17			0.809	0.402	90	123
2	DUB 159	Untested Welded U-Bend	Aged LTCTF SAW	3.55	4.17			0.809	0.402	90	387
9	DEA 2797	MA Alloy 22 Rod	Fresh SAW	2.78	2.8			0.782	0.4	90	401
9	DEA 2853	MA Alloy 22 Rod	Fresh SAW	2.78	2.8			0.782	0.4	90	400
9	DEA 2881	MA Alloy 22 Rod	Fresh SAW	2.78	2.8			0.782	0.4	90	401
9	DEA 2928	MA Alloy 22 Rod	Fresh SAW	2.78	2.8			0.782	0.4	90	401
9	DEA 2940	MA Alloy 22 Rod	Fresh SAW	2.78	2.8			0.782	0.4	90	401
9	DEA 3010	MA Alloy 22 Rod	Fresh SAW	2.78	2.8			0.782	0.4	90	401
9	DEA 3014	MA Alloy 22 Rod	Fresh SAW	2.78	2.8			0.782	0.4	90	398
9	DEA 3082	MA Alloy 22 Rod	Fresh SAW	2.78	2.8			0.782	0.4	90	400
10	DEA 2850	MA Alloy 22 Rod	Aged LTCTF SAW	3.67	3.83			0.838	0.426	90	387
10	DEA 2851	MA Alloy 22 Rod	Aged LTCTF SAW	3.67	3.83			0.838	0.426	90	382
10	DEA 2852	MA Alloy 22 Rod	Aged LTCTF SAW	3.67	3.83			0.838	0.426	90	376
10	DEA 2854	MA Alloy 22 Rod	Aged LTCTF SAW	3.67	3.83			0.838	0.426	90	383
10	DEA 2855	MA Alloy 22 Rod	Aged LTCTF SAW	3.67	3.83			0.838	0.426	90	385
10	DEA 2856	MA Alloy 22 Rod	Aged LTCTF SAW	3.67	3.83			0.838	0.426	90	375
10	DEA 2857	MA Alloy 22 Rod	Aged LTCTF SAW	3.67	3.83			0.838	0.426	90	378
10	DEA 2858	MA Alloy 22 Rod	Aged LTCTF SAW	3.67	3.83			0.838	0.426	90	383
1	DUB 028	LTCTF Welded U-Bend	Aged LTCTF SAW	2.98	3.14			0.765	0.372	60	380

Table O-3. Long-Term Corrosion Potential Measurements (Continued)

Cell No.	Sample ID	Sample Type	Solution	pH Before	pH After	Calculated Composition		Measured Composition		Temp (°C)	E_{corr} (mV vs. Ag/AgCl)
						Cl (mol/kg)	NO ₃ (mol/kg)	Cl (mol/kg)	NO ₃ (mol/kg)		
1	DUB 157	Untested Welded U-Bend	Aged LTCTF SAW	2.98	3.14			0.765	0.372	60	408
7N or 7-2	DEA 2802	MA Alloy 22 Rod	Aged LTCTF SAW	3.72	3.88			0.808	0.408	25	265
7N or 7-2	DEA 2807	MA Alloy 22 Rod	Aged LTCTF SAW	3.72	3.88			0.808	0.408	25	258
7N or 7-2	DEA 2859	MA Alloy 22 Rod	Aged LTCTF SAW	3.72	3.88			0.808	0.408	25	241
5	DUB 128	LTCTF Welded U-Bend	Aged LTCTF SDW	9.55	9.66			0.0033	0.000973	60	54.2
5	DUB 150	Untested Welded U-Bend	Aged LTCTF SDW	9.55	9.66			0.0033	0.000973	60	31.1
17	DEA 2813	MA Alloy 22 Rod	SAW without Silicate	2.5	2.97					90	410
17	DEA 2814	MA Alloy 22 Rod	SAW without Silicate	2.5	2.97					90	409
17	DEA 2815	MA Alloy 22 Rod	SAW without Silicate	2.5	2.97					90	408
17	JE2042	ASW Alloy 22 Rod	SAW without Silicate	2.5	2.97					90	414
17	JE2043	ASW Alloy 22 Rod	SAW without Silicate	2.5	2.97					90	414
17	JE2044	ASW Alloy 22 Rod	SAW without Silicate	2.5	2.97					90	414
17	JE2014	WPA Alloy 22 Rod	SAW without Silicate	2.5	2.97					90	416
17	JE2015	WPA Alloy 22 Rod	SAW without Silicate	2.5	2.97					90	416
17	JE2016	WPA Alloy 22 Rod	SAW without Silicate	2.5	2.97					90	416

Source: Calculated compositions: DTN: LL030703723121.031; Measured compositions: DTN: LL031001023121.035; E_{corr} , pH, and temperature from DTN: LL040402112251.083.

NOTE: Some values are rounded for the table.

Table O-1 shows that the steady-state E_{corr} for Alloy 22 in the acidic SAW at 90°C was on the order of 400 mV versus Ag/AgCl and closer to the platinum electrode. The E_{corr} of Alloy 22 in SAW increased slowly with time, and in approximately 3 months it reached the reported value and then remained steady for more than three years. Some of the cells in Table O-1 were tested for more than 1,000 days. The high anodic value of E_{corr} of Alloy 22 in SAW indicates that the alloy is covered with a protective passive oxide film. In the alkaline solutions, such as SCW and BSW, the E_{corr} of Alloy 22 rods is negative and approximately -200 mV (Table O-1). In the alkaline solutions, the values of E_{corr} for Alloy 22 are lower than the values of E_{corr} for platinum.

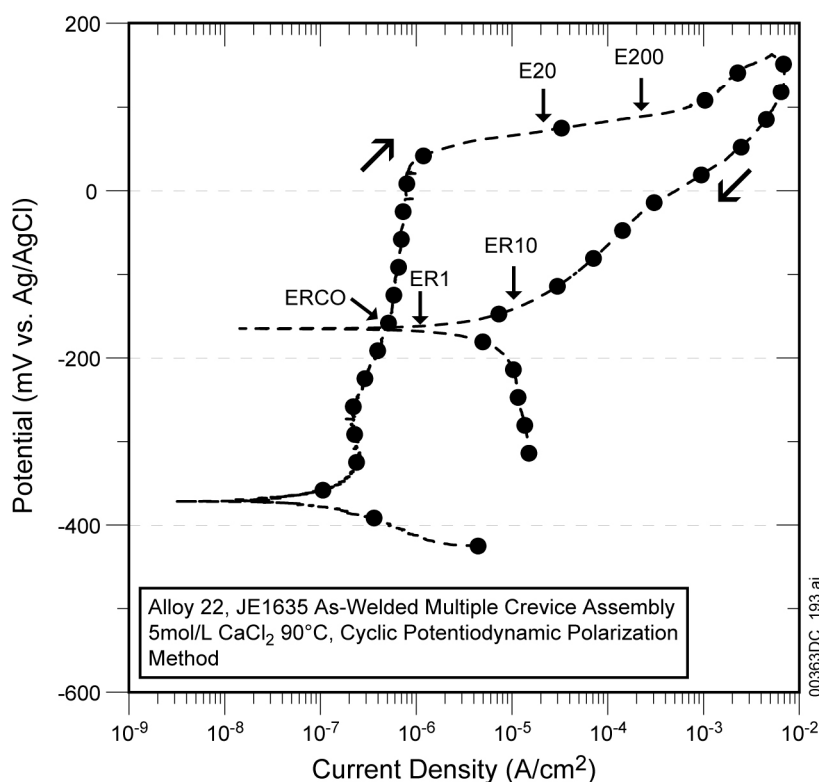
Table O-2 shows the E_{corr} values for Alloy 22 and platinum in pure chloride solutions and in chloride solutions containing different amounts of nitrate additions. In the pure chloride solutions, E_{corr} for mill-annealed Alloy 22 rods is negative, and it is assumed that the alloy remains active and free from passivation. The value of E_{corr} for 4 mol/L NaCl solution at 90°C (Cell 18, Table O-2) is -160 mV versus Ag/AgCl, which is similar to the value of -150 mV versus saturated calomel electrode (SCE) reported for creviced Alloy 22 in 4 mol/L NaCl at 95°C (Dunn, Yang et al. 2003). When nitrate is added to the solutions, the E_{corr} of Alloy 22 increases to anodic values (Table O-2, Figure O-1). In general, the higher the nitrate-to-chloride ratio, the higher the E_{corr} (Figure O-1) values are. While as-welded and welded plus aged rods seem to reach the steady-state E_{corr} values in less than 1 month, the E_{corr} values for some mill-annealed Alloy 22 electrodes may take more than 1 year to stabilize. Table O-2 also shows that the E_{corr} of welded plus aged rods had a higher E_{corr} even in pure chloride solutions, indicating partial passivation.

The shift of E_{corr} in time depends on the environmental conditions (including electrolyte composition and temperature). In most systems, E_{corr} seems to be stable at testing times of 100 days (3 months). In some systems, the stabilization of E_{corr} occurs in 1 week and in others (as in Cell 14 in Table O-2), it may take nearly a year. In some systems, the E_{corr} value eventually reaches the laboratory-measured value of E_{crit} . In the drift, this occurrence may indicate that the conditions for the onset of localized corrosion are present. However, $\Delta E = 0$ is a necessary but not a sufficient condition. Some of the additional conditions are the presence of tight crevices and a strong cathodic reaction that would consume the electrons generated by the localized corrosion process. As discussed in Section O.4.3, even in a laboratory test (with an unlimited sink for electrons), crevice corrosion can be initiated but cannot be sustained.

O.4.2 Critical Potential of Alloy 22

E_{crit} is defined as a potential above which localized corrosion occurs. In general terms, localized corrosion could be crevice corrosion or pitting corrosion. The following three variables control the occurrence of localized corrosion: chloride concentration, temperature, and applied potential. The higher the values of these variables, the more susceptible the alloy is to localized corrosion. Alloy 22 is resistant to pitting corrosion but is susceptible to crevice corrosion under conditions of high temperature, high chloride concentration, and high applied potentials. The susceptibility of Alloy 22 to crevice corrosion also depends on the geometry (tightness) of the crevice and the crevicing material. At different chloride concentrations and temperatures, Alloy 22 has different values of E_{crit} . The value of E_{crit} can be measured using cyclic potentiodynamic polarization, according to ASTM G 61-86, *Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, and Cobalt-*

Based Alloys, or other methods, such as potentiostatic tests or the Tsujikawa Hisamatsu electrochemical method (Akashi et al. 1998). In the cyclic potentiodynamic polarization test, the potential starts in the vicinity of the open circuit potential and increases at a constant rate until a predetermined current density is attained. Then, the potential is decreased at the same rate until repassivation of the test specimen occurs. In the potentiostatic test, a fixed potential is applied and the output current density is monitored as a function of time. In the Tsujikawa Hisamatsu electrochemical test, a combination between potentiodynamic, galvanostatic, and potentiostatic treatments is applied to the test specimen. Figure O-2 shows a cyclic potentiodynamic polarization test for creviced Alloy 22 in a hot chloride solution showing several characteristic potentials from the curve. A popular method to assess E_{crit} is to equate it to the repassivation potential in a cyclic potentiodynamic polarization curve (Figure O-2). The repassivation potential can be defined as ERCO (the potential at which the forward and reverse scan are intersected) or ER1 (the potential at which the reverse scan reaches a current density of $1 \mu\text{A}/\text{cm}^2$). Figure O-2 shows that the values of ER1 (-162 mV) and ERCO (-164 mV) are similar.



Source: DTN: LL040402212251.084.

Figure O-2. Cyclic Potentiodynamic Polarization of As-Welded Alloy 22 Multiple Crevice Assembly in 5 mol/L CaCl_2 at 90°C

Table O-4 shows that the repassivation potential (ER1) of creviced Alloy 22 in 5 mol/L CaCl_2 at 90°C for welded and base metal are about the same at approximately -180 mV . Table O-4 also shows that the repassivation potential measured using cyclic potentiodynamic polarization (ERCO) and Tsujikawa Hisamatsu electrochemical tests (ERCREV) are similar (-164 and -130 mV , respectively). The values of E_{crit} obtained using cyclic potentiodynamic polarization

tests are slightly lower (more conservative) than the values obtained using Tsujikawa Hisamatsu electrochemical tests. In Table O-4, E20 and E200 are breakdown potentials and ER10, ER1, ER0 and ER,CREV are repassivation potentials. The potential used as E_{crit} is ER0. A larger set of critical potential data is shown in Table O-5.

Table O-4. Repassivation Potential for Alloy 22 Measured Using Cyclic Potentiodynamic Polarization and Tsujikawa Hisamatsu Electrochemical Methods

Specimen ID	Type of Specimen and Material	E_{corr} , 24 hours (mV vs. Ag/AgCl)	E20 CPP (mV vs. Ag/AgCl)	E200 CPP (mV vs. Ag/AgCl)	ER10 CPP (mV vs. Ag/AgCl)	ER1 CPP (mV vs. Ag/AgCl)	ER0 CPP (mV vs. Ag/AgCl)	ER,CREV THE (mV vs. Ag/AgCl)
JE1607	MCA, Welded	-345	NA	NA	NA	NA	NA	-129
JE1608	MCA, Welded	-310	NA	NA	NA	NA	NA	-127
JE1628	MCA, Welded	-344	NA	NA	NA	NA	NA	-131
JE1629	MCA, Welded	-339	NA	NA	NA	NA	NA	-125
JE1630	MCA, Welded	-340	NA	NA	NA	NA	NA	-133
JE1632	MCA, Welded	-337	NA	NA	NA	NA	NA	-133
DEA3216	MCA, Base	-349	105	128	-136	-182	-200	NA
DEA3217	MCA, Base	-312	47	130	-115	-174	-129	NA
DEA3218	MCA, Base	-368	-49	151	-147	-193	-141	NA
DEA3219	MCA, Base	-342	146	175	-113	-180	-148	NA
JE0037	MCA, Welded	-253	152	160	-140	-184	-195	NA
JE0038	MCA, Welded	-313	129	175	-138	-175	-163	NA
JE0039	MCA, Welded	-286	114	139	-131	-181	-175	NA
JE1635	MCA, Welded	-335	71	88	-142	-162	-164	NA
Avg. $\pm\sigma$	NA	-327 \pm 28	89 \pm 62	143 \pm 27	-133 \pm 12	-179 \pm 8	-164 \pm 23	-130 \pm 3

Source: DTN: LL040402212251.084.

NOTE: THE = Tsujikawa Hisamatsu electrochemical method; CPP = cyclic potentiodynamic polarization method; MCA = multiple crevice assembly.

Table O-5. Critical Potential Measurements (24 hours)

Specimen ID	Data File Prefix	Electrolyte	pH Initial	Test Temp. (°C)	E_{corr} 24 hr (mV)	ER1 (V vs. Ag/AgCl) at 10^{-6} Acm^{-2}	ERCO (V vs. Ag/AgCl)
JE1771	SKG1	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	5.53	60	-402	0.102	-0.007
JE1772	SKG2	6 mol/kg NaCl + 3 mol/kg KNO ₃	5.36	60	-436	0.588	N/A
JE1773	SKG3	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	5.49	100	-524	-0.068	-0.085
JE1774	SKG4	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	5.37	60	-474	0.529	N/A
JE1775	SKG5	6 mol/kg NaCl + 3 mol/kg KNO ₃	5.36	80	-391	0.531	N/A
JE3201	SKG6	6 mol/kg NaCl + 0.3 mol/kg KNO ₃	5.4	100	-531	-0.085	-0.088
JE3202	SKG7	1 mol/kg NaCl + 0.5 mol/kg KNO ₃	5.32	100	-470	0.255	0.254
JE3203	SKG9	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	5.37	80	-478	0.187	0.027
JE3204	SKG8	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	5.49	60	-462	-0.021	-0.073
JE3205	SKG10	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	5.13	60	-471	0.318	0.303
JE3206	SKG11	3.5 mol/kg NaCl + 1.75 mol/kg KNO ₃	5.49	80	-466	0.291	0.290
JE3207	SKG12	3.5 mol/kg NaCl + 1.75 mol/kg KNO ₃	5.49	100	-446	0.379	N/A
JE3208	SKG13	3.5 mol/kg NaCl + 1.75 mol/kg KNO ₃	5.49	100	-498	0.312	0.319
JE3209	SKG14	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	5.38	60	-348	0.151	0.094
JE3210	SKG15	6 mol/kg NaCl + 0.3 mol/kg KNO ₃	5.4	60	-481	0.057	-0.018
JE3211	SKG16	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	5.49	60	-467	0.300	0.269
JE3212	SKG17	1 mol/kg NaCl + 0.5 mol/kg KNO ₃	5.32	60	-437	0.364	0.349
JE3213	SKG18	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	5.13	80	-494	0.289	0.290
JE3214	SKG19	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	5.13	60	-373	0.531	0.550
JE3215	SKG20	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	5.37	100	-505	-0.075	-0.085
JE3216	SKG21	1 mol/kg NaCl + 0.5 mol/kg KNO ₃	5.32	60	-375	0.504	N/A
JE3217	SKG22	6 mol/kg NaCl + 0.3 mol/kg KNO ₃	5.4	80	-472	-0.058	-0.095
JE3218	SKG23	1 mol/kg NaCl + 0.5 mol/kg KNO ₃	5.32	80	-462	0.312	0.305
JE3219	SKG24	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	5.13	80	-460	0.319	0.330
JE3220	SKG25	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	5.13	100	-497	0.021	0.015
JE3221	SKG26	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	5.53	100	-553	-0.119	-0.132
JE3222	SKG27	3.5 mol/kg NaCl + 1.75 mol/kg KNO ₃	5.49	60	-373	0.537	0.520
JE3223	SKG28	6 mol/kg NaCl + 0.3 mol/kg KNO ₃	5.4	100	-507	-0.114	-0.120
JE3224	SKG29	6 mol/kg NaCl + 3 mol/kg KNO ₃	5.36	100	-298	0.308	0.298
JE3225	SKG30	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	5.38	100	-526	-0.104	-0.119
JE3226	SKG31	6 mol/kg NaCl + 3 mol/kg KNO ₃	5.36	60	-368	0.369	N/A
JE3227	SKG32	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	5.38	80	-438	0.021	-0.052
JE3228	SKG33	6 mol/kg NaCl + 0.3 mol/kg KNO ₃	5.4	80	-502	-0.061	-0.097
JE3229	SKG34	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	5.49	80	-477	0.346	0.322
JE3230	SKG35	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	5.49	60	-403	0.549	0.565
JE3231	SKG36	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	5.49	80	-371	0.474	0.489
JE3232	SKG37	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	5.53	80	-489	-0.051	-0.079
JE3233	SKG38	1 mol/kg NaCl + 0.5 mol/kg KNO ₃	5.32	80	-413	0.345	0.344
JE3234	SKG39	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	5.53	80	-483	-0.057	-0.085
JE3235	SKG40	1 mol/kg NaCl + 0.5 mol/kg KNO ₃	5.32	100	-451	0.356	0.365
JE3236	SKG41	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	5.38	100	-505	-0.116	-0.122
JE3237	SKG42	1 mol/kg NaCl + 0.15 mol/kg KNO ₃	5.13	100	-513	-0.050	-0.065
JE3238	SKG43	6 mol/kg NaCl + 3 mol/kg KNO ₃	5.36	80	-491	0.306	0.286
JE3239	SKG44	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	5.53	100	-411	-0.101	-0.104

Table O-5. Critical Potential Measurements (24 hours) (Continued)

Specimen ID	Data File Prefix	Electrolyte	pH Initial	Test Temp. (°C)	E_{corr} 24 hr (mV)	ER1 (V vs. Ag/AgCl) at 10^{-6} Acm^{-2}	ERCO (V vs. Ag/AgCl)
JE3240	SKG45	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	5.37	100	-340	-0.022	-0.040
JE3241	SKG46	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	5.38	60	-360	0.363	0.348
JE3242	SKG47	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	5.49	100	-285	-0.062	-0.096
JE3243	SKG48	3.5 mol/kg NaCl + 1.75 mol/kg KNO ₃	5.49	60	-495	0.321	0.303
JE3244	SKG49	1 mol/kg NaCl + 0.05 mol/kg KNO ₃	5.38	80	-499	0.047	0.026
JE3245	SKG50	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	5.37	60	-510	0.356	0.350
JE3246	SKG51	3.5 mol/kg NaCl + 1.75 mol/kg KNO ₃	5.49	80	-493	0.349	N/A
JE3247	SKG52	6 mol/kg NaCl + 3 mol/kg KNO ₃	5.36	100	-289	N/A	N/A
JE3248	SKG53	6 mol/kg NaCl + 0.9 mol/kg KNO ₃	5.37	80	-529	0.319	0.311
JE3249	SKG54	6 mol/kg NaCl + 0.3 mol/kg KNO ₃	5.4	60	-461	0.368	N/A
JE3250	SKG55	3.5 mol/kg NaCl + 0.175 mol/kg KNO ₃	5.53	60	-525	N/A	N/A
JE3251	SKG56	6 mol/kg NaCl + 3 mol/kg KNO ₃	5.36	60	-505	N/A	N/A
JE3252	SKG57	5.8 mol/kg NaCl + 2.4 mol/kg NaNO ₃ + 18.2 mol/kg KNO ₃	N/A	100	-499	0.485	N/A
JE3253	SKG58	5.8 mol/kg NaCl + 2.4 mol/kg NaNO ₃ + 18.2 mol/kg KNO ₃	N/A	100	-518	0.478	N/A
JE3254	SKG59	5.8 mol/kg NaCl + 2.4 mol/kg NaNO ₃ + 18.2 mol/kg KNO ₃	N/A	115	-373	0.261	N/A
JE3255	SKG60	5.8 mol/kg NaCl + 2.4 mol/kg NaNO ₃ + 18.2 mol/kg KNO ₃	N/A	115	-271	0.154	N/A
JE3256	SKG61	3.5 mol/kg NaCl + 0.525 mol/kg KNO ₃	5.49	60	-498	N/A	N/A
JE3257	SKG62	3.5 mol/kg NaCl + 1.75 mol/kg KNO ₃	5.49	60	-183	N/A	N/A
JE3258	SKG63	3.5 mol/kg NaCl + 0.175 mol/kg NaNO ₃ + 0.35 mol/kg MgSO ₄	N/A	80	-454	0.094	N/A
JE3259	SKG64	3.5 mol/kg NaCl + 0.175 mol/kg NaNO ₃ + 0.35 mol/kg MgSO ₄	N/A	80	-471	-0.401	0.110
JE3260	SKG65	3.5 mol/kg NaCl + 0.175 mol/kg NaNO ₃ + 0.70 mol/kg MgSO ₄	N/A	80	-296	0.066	-0.010
JE3261	SKG66	3.5 mol/kg NaCl + 0.175 mol/kg NaNO ₃ + 0.70 mol/kg MgSO ₄	N/A	80	-426	0.054	0.028
JE3262	SKG67	3.5 mol/kg NaCl + 0.175 mol/kg NaNO ₃ + 1.75 mol/kg MgSO ₄	N/A	80	-387	0.434	0.485
JE3263	SKG68	3.5 mol/kg NaCl + 0.175 mol/kg NaNO ₃ + 1.75 mol/kg MgSO ₄	N/A	80	-465	0.428	0.461
JE3264	SKG69	3.5 mol/kg NaCl + 0.35 mol/kg KNO ₃	5.59	80	-549	0.105	0.055
JE3265	SKG70	3.5 mol/kg NaCl + 0.35 mol/kg KNO ₃	5.59	80	-551	0.269	N/A
JE3266	SKG71	3.5 mol/kg NaCl + 0.70 mol/kg KNO ₃	5.52	80	-516	0.283	0.290
JE3267	SKG72	3.5 mol/kg NaCl + 0.70 mol/kg KNO ₃	5.52	80	-516	0.319	0.323
JE3268	SKG73	3.5 mol/kg NaCl + 1.05 mol/kg KNO ₃	5.59	80	-469	0.362	0.378
JE3269	SKG74	3.5 mol/kg NaCl + 1.05 mol/kg KNO ₃	5.59	80	-539	0.261	0.256
JE3270	SKG75	10 mol/kg CaCl ₂ + 0.5 mol/kg Ca(NO ₃) ₂	N/A	100	-240	-0.038	-0.039
JE3271	SKG76	12 mol/kg CaCl ₂ + 6 mol/kg Ca(NO ₃) ₂	N/A	130	-4	N/A	N/A
JE3272	SKG77	12 mol/kg CaCl ₂ + 1.8 mol/kg Ca(NO ₃) ₂	N/A	130	47	0.013	0.013
JE3273	SKG78	12 mol/kg CaCl ₂ + 1.8 mol/kg Ca(NO ₃) ₂	N/A	130	61	0.017	0.017
JE3274	SKG79	18 mol/kg CaCl ₂ + 0.9 mol/kg Ca(NO ₃) ₂	N/A	160	-24	0.011	0.011
JE3275	SKG80	18 mol/kg CaCl ₂ + 9 mol/kg Ca(NO ₃) ₂	N/A	160	277	N/A	N/A
JE3276	SKG81	10 mol/kg CaCl ₂ + 1.5 mol/kg Ca(NO ₃) ₂	N/A	100	71	0.015	0.013
JE3277	SKG82	12 mol/kg CaCl ₂ + 0.6 mol/kg Ca(NO ₃) ₂	N/A	130	-180	-0.039	-0.040
JE3278	SKG83	12 mol/kg CaCl ₂ + 0.6 mol/kg Ca(NO ₃) ₂	N/A	130	-173	-0.039	-0.039

Table O-5. Critical Potential Measurements (24 hours) (Continued)

Specimen ID	Data File Prefix	Electrolyte	pH Initial	Test Temp. (°C)	E_{corr} 24 hr (mV)	ER1 (V vs. Ag/AgCl) at 10^{-6} Acm ⁻²	ERCO (V vs. Ag/AgCl)
JE3279	SKG84	12 mol/kg CaCl ₂ + 6 mol/kg Ca(NO ₃) ₂	N/A	130	274	N/A	N/A
JE3280	SKG85	18 mol/kg CaCl ₂ + 2.7 mol/kg Ca(NO ₃) ₂	N/A	160	51	0.174	0.239
JE3281	SKG86	18 mol/kg CaCl ₂ + 9 mol/kg Ca(NO ₃) ₂	N/A	160	441	0.698	N/A
JE3282	SKG87	18 mol/kg CaCl ₂ + 0.9 mol/kg Ca(NO ₃) ₂	N/A	160	-1	0.007	0.007
JE3283	SKG88	18 mol/kg CaCl ₂ + 2.7 mol/kg Ca(NO ₃) ₂	N/A	160	36	0.067	0.064
JE3284	SKG89	10 mol/kg CaCl ₂ + 0.5 mol/kg Ca(NO ₃) ₂	N/A	100	-238	-0.042	-0.041
JE3285	SKG90	10 mol/kg CaCl ₂ + 1.5 mol/kg Ca(NO ₃) ₂	N/A	100	-198	0.009	0.018
JE3287	SKG92	10 mol/kg CaCl ₂ + 5 mol/kg Ca(NO ₃) ₂	N/A	100	-89	0.691	N/A
JE3288	SKG93	0.01 mol/kg NaCl + 0.001 mol/kg NaHCO ₃	7.78	80	-555	0.069	0.044
JE3289	SKG94	0.01 mol/kg NaCl + 0.001 mol/kg NaHCO ₃	7.78	80	-611	0.328	N/A
JE3290	SKG95	0.1 mol/kg NaCl + 0.001 mol/kg NaHCO ₃	7.62	80	-271	-0.040	-0.092
JE3291	SKG96	0.1 mol/kg NaCl + 0.001 mol/kg NaHCO ₃	7.62	80	-637	0.032	0.014
JE3292	SKG101	22.5 mol/kg Ca(NO ₃) ₂ + 0.225 mol/kg MgCl ₂	N/A	145	243	0.593	N/A
JE3293	SKG97	0.01 mol/kg NaCl + 0.001 mol/kg NaHCO ₃	7.78	95	-710	-0.021	-0.023
JE3294	SKG98	0.01 mol/kg NaCl + 0.001 mol/kg NaHCO ₃	7.78	95	-238	0.041	0.028
JE3295	SKG99	0.1 mol/kg NaCl + 0.001 mol/kg NaHCO ₃	7.62	95	-441	-0.097	-0.132
JE3296	SKG100	0.1 mol/kg NaCl + 0.001 mol/kg NaHCO ₃	7.62	95	-223	-0.077	-0.133
JE3297	SKG102	22.5 mol/kg Ca(NO ₃) ₂ + 0.225 mol/kg MgCl ₂	N/A	145	624	0.791	0.781
JE3298	SKG104	15 mol/kg Ca(NO ₃) ₂ + 1.5 mol/kg CaCl ₂	N/A	125	348	N/A	N/A
JE3299	SKG105	15 mol/kg Ca(NO ₃) ₂ + 1.5 mol/kg CaCl ₂	N/A	125	357	0.709	0.740
JE3300	SKG103	5 mol/kg Ca(NO ₃) ₂ + 5 mol/kg CaCl ₂	2.37*	100	116	0.558	N/A

Source: DTNs: LL040307212251.080 (pH and temperature data); LL040402212251.084 (all other data).

NOTE: Tests were run on welded samples, with multiple crevice assembly specimen geometry, and SiC 600 grit surface preparation. Open-circuit potential measured at 24th hour of exposure.

O.4.3 Margin of Safety for Alloy 22

Table O-6 shows the 24-hour and the long-term E_{corr} for Alloy 22 in pure NaCl and CaCl₂ solutions and in solutions containing oxyanions, such as sulfate, silicate, and nitrate. Table O-6 also shows the E_{crit} potential for localized corrosion (ERCO) and the ΔE values. Table O-6 shows that when tests were carried out in hot concentrated and pure chloride solutions, the margin against localized corrosion is small. When Alloy 22 mill-annealed rods were removed from Cell 8 (Table O-2) after more than 600 days of testing, all five specimens showed pitting corrosion. The E_{corr} of these rods was steady at -130 mV versus Ag/AgCl (Tables O-2 and O-6). The pits were covered with a glassy black oxide and appeared to be nonactive. Studies are underway to determine the extent of this pitting corrosion. In another test (Cell 20, Table O-2), mill-annealed and as-welded multiple crevice assembly specimens were removed from testing after 200 days. Both specimens exhibited crevice corrosion. The E_{corr} of both specimens was

–100 mV. These tests show that localized corrosion can be initiated in bulk-aerated concentrated CaCl_2 brines at high temperature (120°C). Rod specimens (mill-annealed, as-welded, and welded plus aged) were removed from Cell 18 (aerated 4 mol/L NaCl at 90°C, Table O-2) after more than 300 days of testing. None of these noncreviced rods showed any type of localized corrosion, in spite of the fact that Table O-6 shows that ΔE could be near 0 for mill-annealed creviced specimens. Table O-6 also shows that when nitrate is added to hot concentrated brines (NaCl and CaCl_2), the ΔE becomes positive, which is a condition that inhibits localized corrosion.

Table O-6. E_{corr} and E_{crit} for Alloy 22 in Concentrated Brines

Electrolyte	Metallurgical Condition	E_{corr} (24 hours) Deaerated (mV)	E_{corr} (>100 days) Aerated (mV)	E_{crit} (ERCO) (mV)	ΔE (mV)
4 mol/L (4.4 mol/kg Cl^-) NaCl, 90°C to 95°C	Mill-Annealed	–320	–160	–170	150 to <0
	As-Welded	–240	–100	–160	80 to <0
5 mol/L CaCl_2 (12 mol/kg Cl^-), 120°C	As-Welded	–350	–40	–180	170 to <0
	Mill-Annealed (Rod)	–380	–130	–130	250 to 0
5 mol/L CaCl_2 (12 mol/kg Cl^-), 90°C	As-Welded	–280	NA	–180	≤ 100
5 mol/L CaCl_2 (13 mol/kg Cl^-) + 0.5 mol/L $\text{Ca}(\text{NO}_3)_2$ (7 mol/kg NO_3^-), 90°C	Mill-Annealed	–370	10	310	300 to 680

Source: DTN: LL040402212251.084.

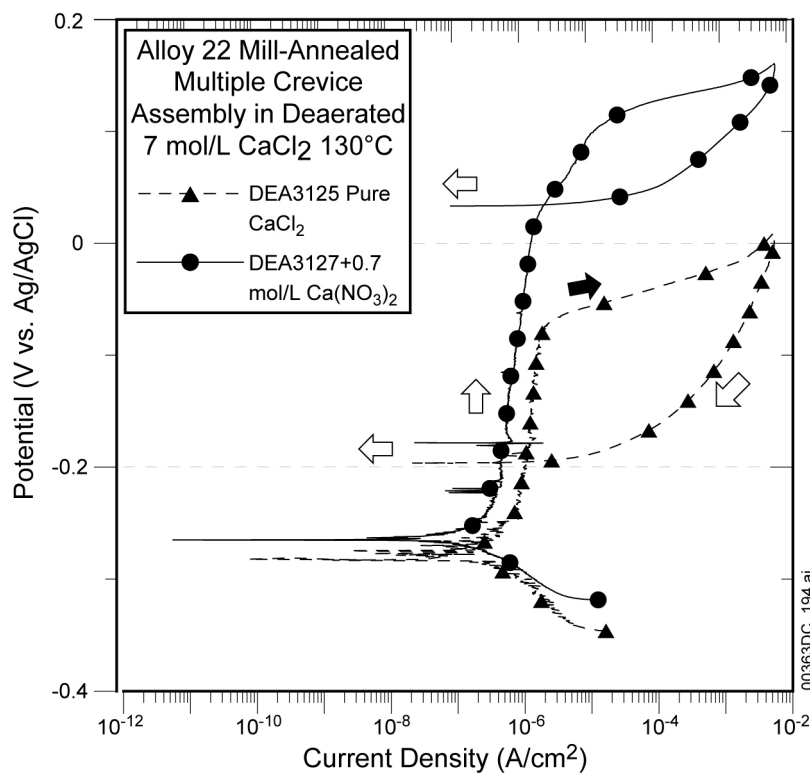
NOTE: All the specimens were creviced except for the rods.

Constant potential tests of creviced specimens in 5 mol/L CaCl_2 solution at 120°C for 1 week (168 hours) showed that Alloy 22 was susceptible to crevice corrosion at –100 mV versus Ag/AgCl but did not suffer localized attack at –200 mV, confirming the results from the long-term E_{corr} tests in Table O-6.

O.4.4 Inhibitive Effect of Nitrate for Alloy 22

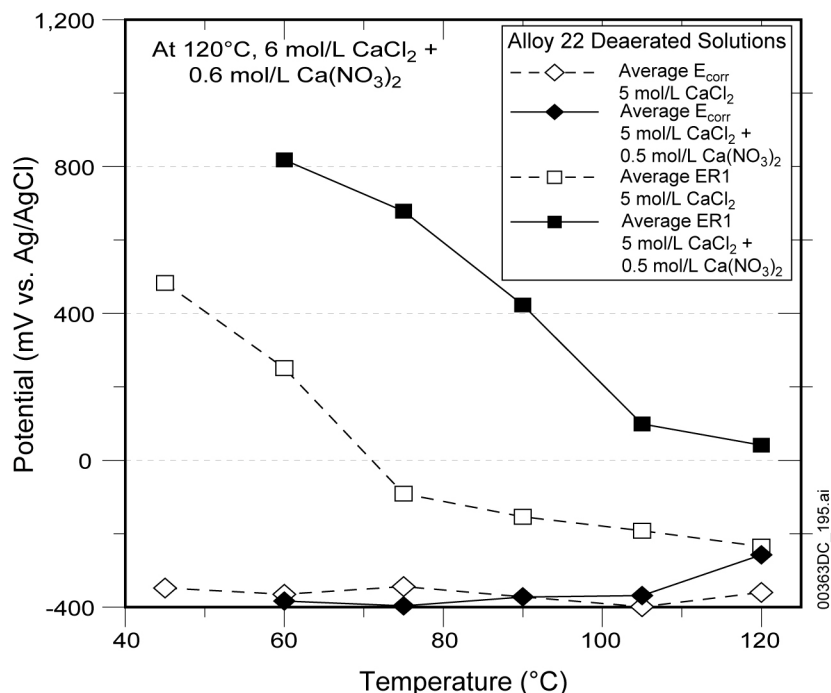
Nitrate is a strong inhibitor of localized corrosion in hot chloride solutions (Kehler et al. 2001; Dunn and Brossia 2002; Evans and Rebak 2002; Evans et al. 2003). Figure O-3 shows the cyclic potentiodynamic polarization curves for mill-annealed Alloy 22 in concentrated CaCl_2 solution at 130°C and the effect of adding nitrate (Evans et al. 2003). The passive current density of Alloy 22 in the nitrate-containing solution was lower than in the pure CaCl_2 solution (Figure O-3). The presence of nitrate also raised the breakdown potential and the repassivation potential. Figure O-4 shows the average 24-hour E_{corr} and the repassivation potentials (ER1) for Alloy 22 in 5 mol/L CaCl_2 and 5 mol/L CaCl_2 + 0.5 mol/L $\text{Ca}(\text{NO}_3)_2$ as a function of the temperature (Evans et al. 2003). For the temperature range 60°C to 120°C, ER1 for nitrate-containing solutions was higher than for pure chloride solutions (Figure O-4). The difference of ER1 less the E_{corr} (ΔE) was positive for all temperatures, both for pure chloride solutions and solutions containing nitrate, even though this difference was larger for those containing nitrate

(Figure O-4). For example, at 90°C, ΔE was approximately 800 mV for the nitrate-containing brine and approximately 200 mV for the pure chloride solution.



Source: Evans et al. 2003, Figure 10.

Figure O-3. Effect of Nitrate on the Anodic Polarization of Alloy 22



Source: Evans et al. 2003, Figure 13.

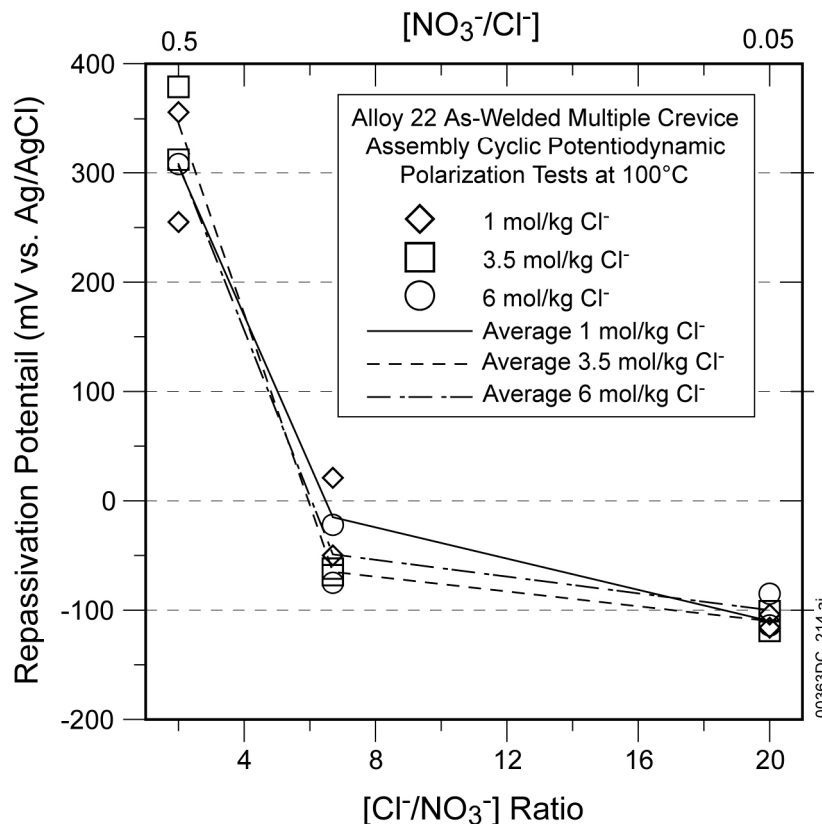
Figure O-4. Effect of Nitrate on the Repassivation Potential of Alloy 22

Tests were conducted to study the effect of nitrate in Cl^- electrolytes on the critical potential for localized corrosion of Alloy 22 in several solutions containing different amounts of NaCl and KNO_3 (Table O-7). The salts were mixed with NO_3^-/Cl^- ratios of 0.05, 0.15, and 0.5. The testing temperatures were 60°C, 80°C, and 100°C (Table O-7). Results show the beneficial effect of nitrate on inhibiting localized corrosion in Alloy 22. It was also shown that the ratio of NO_3^-/Cl^- and temperature have the dominant effect on the repassivation potential of Alloy 22. The absolute Cl^- concentration has a lower effect on the repassivation potential compared with temperature and the NO_3^-/Cl^- ratio (Table O-7 and Figure O-5). Figure O-5 contains both the average repassivation potential data (lines) and the actual values (symbols). On the other hand, Table O-7 shows only the average values.

Table O-7. Testing Matrix for the Effect of Chloride, Nitrate, and Temperature on the Repassivation Potential for As-Welded Multiple Crevice Assembly Alloy 22 Specimens Measured Using the Cyclic Potentiodynamic Polarization Method

NaCl (Cl ⁻) (m)	KNO ₃ (NO ₃ ⁻) (m)	Cl ⁻ /NO ₃ ⁻	NO ₃ ⁻ /Cl ⁻	Temp. (°C)	Average E_{corr} , 24 hours (mV vs. Ag/AgCl)	Average ER1 (mV vs. Ag/AgCl)	Average ERCO (mV vs. Ag/AgCl)
1	0.05	20.0	0.05	60	-354	257	221
1	0.15	6.7	0.15	60	-422	425	427
1	0.5	2.0	0.5	60	-406	434	349
1	0.05	20.0	0.05	80	-469	34	-13
1	0.15	6.7	0.15	80	-477	304	310
1	0.5	2.0	0.5	80	-438	329	325
1	0.05	20.0	0.05	100	-516	-110	-121
1	0.15	6.7	0.15	100	-505	-15	-25
1	0.5	2.0	0.5	100	-461	306	310
3.5	0.175	20.0	0.05	60	-432	40.5	-40
3.5	0.525	6.7	0.15	60	-435	424.5	417
3.5	1.75	2.0	0.5	60	-434	429	411.5
3.5	0.175	20.0	0.05	80	-486	-54	-82
3.5	0.525	6.7	0.15	80	-424	410	405.5
3.5	1.75	2.0	0.5	80	-479.5	320	327.5
3.5	0.175	20.0	0.05	100	-482	-110	-118
3.5	0.525	6.7	0.15	100	-404.5	-65	-90.5
3.5	1.75	2.0	0.5	100	-472	345.5	319
6	0.3	20.0	0.05	60	-471	212.5	-18
6	0.9	6.7	0.15	60	-492	442.5	350
6	3	2.0	0.5	60	-402	478.5	NA
6	0.3	20.0	0.05	80	-487	-59.5	-96
6	0.9	6.7	0.15	80	-503.5	253	169
6	3	2.0	0.5	80	-441	418.5	286
6	0.3	20.0	0.05	100	-519	-99.5	-104
6	0.9	6.7	0.15	100	-422.5	-48.5	-62.5
6	3	2.0	0.5	100	-294	308	298

Source: DTN: LL040402212251.084.



Source: DTN: LL040402212251.084.

NOTE: The higher the relative amount of nitrate, the higher the ER1. There is little effect of the total amount of chloride.

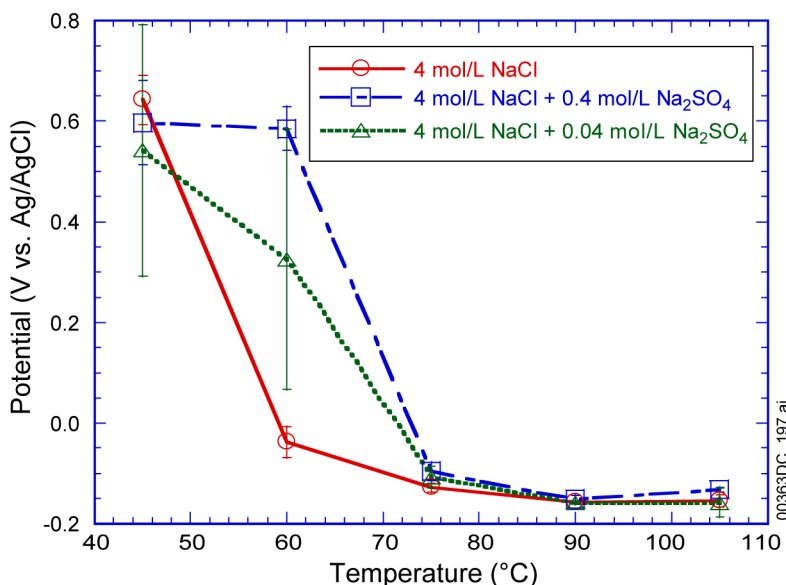
Figure O-5. Repassivation Potential (ER1) for Alloy 22 as a Function of $[\text{NO}_3^-]/[\text{Cl}^-]$ Ratio at 1.0, 3.5, and 6.0 molal $[\text{Cl}^-]$ at 100°C

Potentiostatic tests were conducted in creviced specimens of Alloy 22 exposed to concentrated brines containing chloride and nitrate. For example, a constant potential of +100 mV versus Ag/AgCl was applied to a specimen immersed in 6 mol/kg NaCl + 0.9 mol/kg KNO₃ at 100°C. The specimen suffered crevice corrosion, but the current emanating from the crevice peaked early in the test and then decreased because the crevice corrosion propagation slowed down or stifled. More detailed studies are underway to determine crevice corrosion susceptibility using potentiostatic tests. Results from another test conducted in 3.5 mol/kg NaCl + 0.525 mol/kg KNO₃ at 100°C and at +100 mV versus Ag/AgCl also showed crevice corrosion. These two tests confirm that crevice corrosion will initiate when the applied constant potential is above the repassivation potential (ER1) in Table O-7 and Figure O-5. The presence of nitrate in the drift is highly beneficial because it counteracts the aggressive nature of chloride in hot solutions.

O.4.5 Inhibitive Effect of Sulfate for Alloy 22

The effect of sulfate (SO_4^{2-}) ions on localized corrosion (crevice corrosion) of Alloy 22 was studied for the wrought (base or mill-annealed) condition in 4 mol/L NaCl, 4 mol/L

NaCl + 0.4 mol/L Na₂SO₄, and 4 mol/L NaCl + 0.04 mol/L Na₂SO₄ between 45°C and 105°C using multiple crevice assembly specimens in cyclic potentiodynamic polarization tests. Alloy 22 was susceptible to localized corrosion in 4 mol/L NaCl, 4 mol/L NaCl + 0.04 mol/L Na₂SO₄, and 4 mol/L NaCl + 0.4 mol/L Na₂SO₄ between 45°C and 105°C under anodic polarization conditions. The presence of sulfate slightly increased the resistance of Alloy 22 to crevice corrosion. A higher beneficial effect of sulfate was observed for the higher concentration (0.4 mol/L). The presence of sulfate increased the breakdown potentials at all the tested temperatures and increased the repassivation potentials (ERCO) at 60°C (Figure O-6). There was no improvement in the repassivation potentials at 75°C and higher temperatures (Figure O-6). It is likely that the aggressive effect of the higher temperature overshadowed the beneficial effect of adding sulfate. Localized damage under the crevice former was initiated as small pits, and these pits later coalesced to form shallow trenches. When sulfate was present, crevice corrosion produced smaller pits in the areas of local damage (under the crevice former). As the level of aggressiveness of the environment increased, crevice corrosion tended to proceed away from the crevice formers toward the noncreviced area. The presence of sulfate in the drift may be of no consequence for the lifetime of the waste package in the drift.



Source: DTNs: LL040402212251.084; LL040500312251.087.

NOTE: The inhibitive effect of sulfate is more evident at the intermediate temperature.

Figure O-6. Repassivation Potential for Alloy 22 in Pure NaCl Solution in NaCl + Na₂SO₄ Solutions as a Function of the Temperature

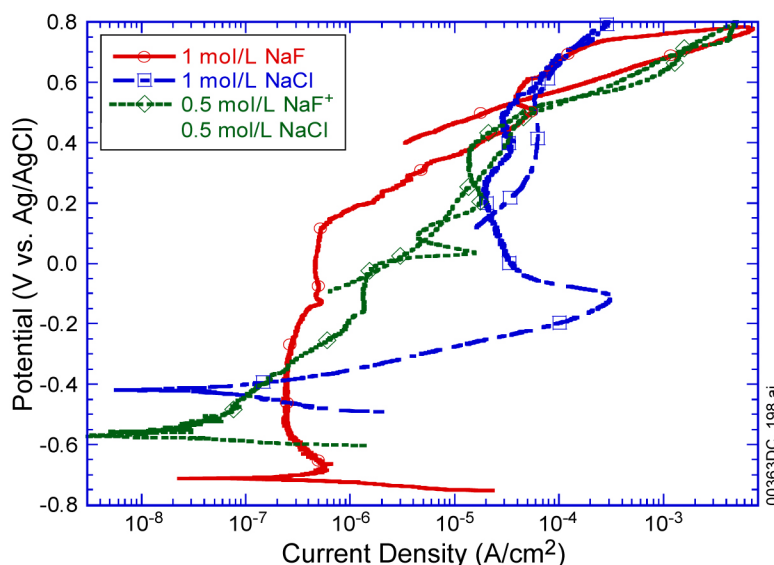
O.4.6 Effect of Carbonate for Alloy 22

Many studies have been conducted on the anodic behavior of Alloy 22 in SCW solution, which is approximately 1,000 times more concentrated than J-13 well water from a well near Yucca Mountain. SCW is rich in carbonate oxyanions (as well as nitrate, sulfate, and silicate) but also contains chloride and fluoride anions. Cyclic potentiodynamic polarization and Tsujikawa Hisamatsu electrochemical tests of creviced Alloy 22 specimens did not show any evidence of

crevice corrosion, even at 100°C. Table O-1 shows that E_{corr} of Alloy 22 in SCW is approximately -200 mV versus Ag/AgCl. When polarized anodically, Alloy 22 shows an intermediate anodic peak in SCW at 90°C at approximately +350 mV versus Ag/AgCl (i.e., the margin of safety ΔE is on the order of 500 mV), which is significant.

O.4.7 Effect of Fluoride for Alloy 22

Initial data have been collected to investigate the effect of fluoride on the breakdown and repassivation potentials for localized corrosion. The localized corrosion behavior of Alloy 22 was studied by using multiple crevice assembly specimens using cyclic potentiodynamic polarization in 1 mol/L NaCl, 1 mol/L NaF, and 0.5 mol/L NaCl + 0.5 mol/L NaF solutions at 60°C and 90°C (Meck et al. 2003; Day et al. 2003). Figure O-7 shows the cyclic potentiodynamic polarization curves for multiple crevice assembly Alloy 22 in the three electrolytes at 90°C. The lowest passive current density corresponded to the 1 mol/L NaF solution. Observations from the tested specimens in 1 mol/L NaCl showed that, at 90°C, they suffered crevice corrosion, while at 60°C, they suffered only transpassive dissolution due to the high applied potentials. None of the multiple crevice assembly specimens tested in 1 mol/L NaF at 60°C and 90°C suffered crevice corrosion. The only mode of corrosion was border corrosion (outside the crevice formers) and transpassive dissolution. For the Alloy 22 tested in the halide mixture (0.5 mol/L NaCl + 0.5 mol/L NaF), most of the specimens suffered crevice corrosion, both at 60°C and 90°C, besides border corrosion and transpassive dissolution. The presence of crevice corrosion in the samples tested in halide mixtures is noteworthy, considering the cyclic potentiodynamic polarization curves at both temperatures showed little or no hysteresis (Meck et al. 2003). The depth of attack at 90°C was more severe in 0.5 mol/L NaF + 0.5 mol/L NaCl than in 1 mol/L NaCl, even though there was less surface per unit area damaged by crevice corrosion. The data available are limited to fully quantify the effect of fluoride, not only in the presence of chloride but of oxyanions, such as nitrate, sulfate, and carbonate. However, as discussed in Section O.4.6, no localized corrosion was observed for Alloy 22 in SCW for temperatures up to 100°C. SCW solution contains 1,400 ppm fluoride and 6,700 ppm chloride. Fluoride is not an influencing anion that impacts the performance of the waste package outer shell. Fluoride forms insoluble salts (e.g., with calcium); therefore, its availability in the drift is limited. The most important anions are chloride (aggressive) and nitrate (inhibitor).

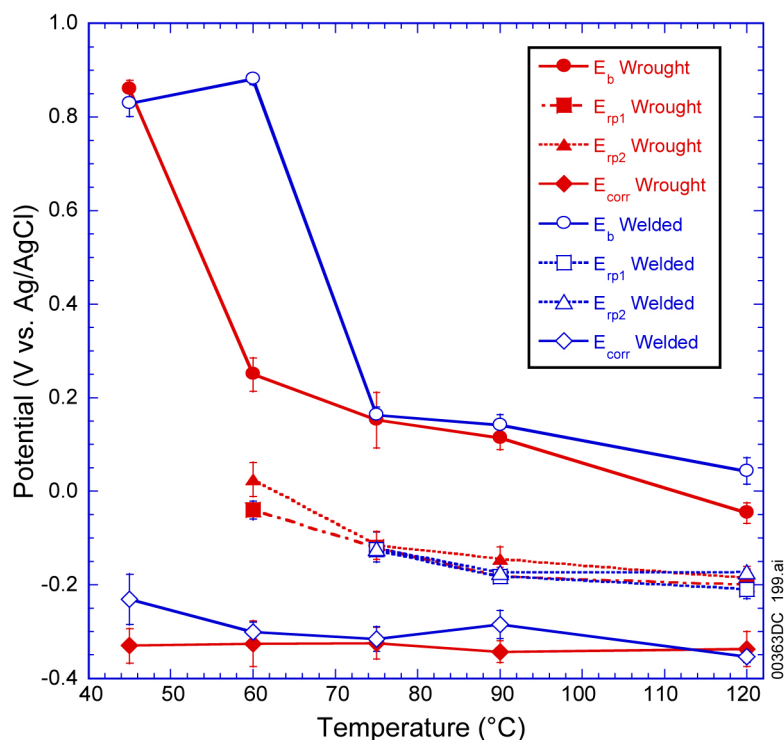


Source: Day et al. 2003, Figure 8.

Figure O-7. Cyclic Potentiodynamic Polarization of Alloy 22 Multiple Crevice Assembly in Deaerated 1 mol/L NaF, 1 mol/L NaCl and 0.5 mol/L NaF + 0.5 mol/L NaCl at 90°C

O.4.8 Effect of Metallurgical Condition on the Critical Potentials for Localized Corrosion of Alloy 22

Comprehensive studies have been carried out in 5 mol/L CaCl_2 to investigate the effect of welding on the susceptibility of Alloy 22 to localized corrosion. Figure O-8 shows that the characteristic potentials for both as-welded and mill-annealed specimens are practically the same. The welded and nonwelded specimens were prepared from thick (greater than 1 in.) plates. After the tests, the specimens showed similar localized corrosion in the base metal and in the welded seam. In many cases, the corrosion attack was more pronounced in the base metal than in the weld seam. Evaluation of the susceptibility of welded and mill-annealed Alloy 22 to crevice corrosion in less concentrated chloride solutions (below 0.1 mol/L chloride) also showed that both welded and base metal materials seem to have the same resistance to attack. Similar behavior was also reported at 95°C for NaCl solutions (Dunn, Cragnolino et al. 2004, Figure 5).



Source: DTNs: LL040402212251.084; LL030400112251.043; LL030406212251.044.

NOTE: E_{rp2} in the figure is ERCO.

Figure O-8. Average Critical Potentials for Breakdown of the Repassivation Potential and the Corrosion Potential as a Function of Temperature for Wrought (Mill-Annealed) and As-Welded Multiple Crevice Assembly Alloy 22 in 5 mol/L CaCl_2

Table O-8 shows a few data on the effects of welding and thermal aging. The thermal aging was carried out at 700°C for 173 hours. In this aged condition, the microstructure of Alloy 22 will have grain boundaries fully decorated with topologically closed packed precipitates. Table O-8 shows very little difference in the anodic behavior between as-welded and welded plus aged materials. As-welded and welded plus aged materials have similar E_{corr} in both solutions (Table O-8). The welded plus aged material seems to have a slightly lower breakdown (E_{200}) and repassivation (E_{R1}) potential than the as-welded material, especially in the solution that contains nitrate. Corroborative tests on the effect of thermal aging in conditions less aggressive than those listed in Table O-8 are planned. Current studies are also underway to study the effect of black annealing and water quenching (after welding) on the localized corrosion resistance of Alloy 22. It has been reported that solution annealing of the welds at 1,125°C for 15 minutes reduces the repassivation potential of Alloy 22 as compared to the as-welded material (Dunn, Cragnolino et al. 2004, Figure 5). The fact that it was reported that solution heat-treated welds may be more susceptible to crevice corrosion than as welded material needs to be corroborated. Nevertheless, solution annealing does not decrease the repassivation potential to an extent limiting the lifetime of the waste package.

It is apparent from the current results that the welded material is not more susceptible to crevice corrosion than the base metal. That is, the fact that the waste package outer shell will be welded is not a limiting factor for the performance of the waste package.

Table O-8. Effects of Thermal Aging of Alloy 22 on Characteristic Potentials from Cyclic Potentiodynamic Polarization

Electrolyte	Metallurgical Condition	24-hour E_{corr} (mV vs. Ag/AgCl)	E200 (mV vs. Ag/AgCl)	ER1 (mV vs. Ag/AgCl)
5 mol/L CaCl_2 , 120°C	As-welded	-353, -376	21, -112	-192, -253
	Welded plus aged	-329, -333	-134, -134	-251, -223
1 mol/L CaCl_2 + 1 mol/L $\text{Ca}(\text{NO}_3)_2$, 105°C	As-welded	-310, -225	585, 620	351, 359
	Welded plus aged	-296, -276	583, 576	193, 208

O.4.9 Heavy Metals Effects

Trace amount of elements, such as lead, arsenic, and mercury, may be present in underground water. The amount of these elements is expected to be negligible since most of them develop insoluble salts with many of the anions available in groundwater.

The effect of lead on the corrosion behavior of Alloy 22 has been studied, both with respect to its effect on localized corrosion and in regard to its influence on environmentally assisted cracking (Estill et al. 2002; Pan et al. 2003; Andresen et al. 2004). Lead had no influence on environmentally assisted cracking (Andresen et al. 2004). Lead only produced increased passive corrosion of Alloy 22 at high concentrations of lead chloride (PbCl_2) and at a pH level of 0.5 (Pan et al. 2003). Andresen et al. (2004) found that the addition of 100 ppm lead as $\text{Pb}(\text{NO}_3)_2$ to 95°C dilute BSW solution decreased the E_{corr} of Alloy 22 after 341 days of exposure from -195 mV (SCE) to -263 mV (SCE). Therefore, the lifetime of the waste package will not be limited by the presence of lead.

The presence of arsenic may promote hydrogen uptake by the metal by poisoning the atomic hydrogen recombination reaction. However, nickel alloys are not very susceptible to hydrogen embrittlement. Therefore, the lifetime of the waste package will not be limited by the presence of arsenic.

The effect of mercury was not studied, due to the absence of mercury in Yucca Mountain environments and because mercury salts are rather insoluble.

O.4.10 Effect of Microbially Influenced Corrosion

One of the many environmental factors that may affect the corrosion performance of an alloy for repository application is microbial activity, which is generally referred to as MIC. MIC is discussed in detail separately in the response to CLST 1.02 (Appendix I). The effect of microorganism activity could be detrimental (as a promoter) to the resistance of the alloy to corrosion. Nickel and titanium alloys, in general, are not highly influenced by MIC (BSC 2003a; BSC 2003b). There are three possible ways by which MIC could affect the corrosion performance of Alloy 22: (1) increasing the general corrosion rate at E_{corr} , (2) increasing the E_{corr} by producing oxidizing species or by promoting the formation of a passivating oxide film

on the alloy, and (3) decreasing the critical potential for localized corrosion (e.g., the breakdown potential, E200, or the repassivation potential, ER1). Currently, there is no published evidence that MIC significantly changes corrosion potentials of Alloy 22 in repository relevant environments. This is also corroborated by the LTCTF data described in response to CLST 1.02 (Appendix I, Section 1.4.3) and discussed below.

Corrosion testing of Alloy 22 and titanium specimens has been ongoing for more than 5 years at the LTCTF at Lawrence Livermore National Laboratory. The tests are being conducted in concentrated brines. While the solutions were not initially sterilized, they were intermittently exposed to ambient air. As a result, there was a potential for the establishment of a microbial community in the test solutions. Indeed, characterization of the solutions showed the presence of heat-tolerant and desiccation-tolerant organisms in the 60°C SDW (pH ~ 10) and SAW (pH ~ 3) which is brine concentrated 100× more than SDW. No active microorganisms were detected in the tanks at 90°C. Heat- and desiccation-tolerant microorganisms were also found in the repository rock samples. It is therefore possible to apply the results of the LTCTF results in a microbe-containing environment to that expected in the repository.

Results of corrosion rate measurements on the 5-year exposed specimens showed that the rates were very low (10 nm/yr and lower) for all specimen configurations (creviced versus uncreviced), exposure environments and material conditions (welded versus base metal). Effects of temperature difference between 90°C (without microbes) and 60°C (with microbes) were also not discernible. These results indicate that the effects of the presence of microbes in the test solutions had no deleterious effects on general corrosion rates. Therefore, the lifetime of the waste package will not be limited by the presence of microbial activity.

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O.5.2 Codes, Standards, and Regulations

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O.5.3 Data, Listed by Data Tracking Number

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