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Alloy 22 Localized Corrosion Susceptibility In Aqueous Solutions Of Chloride And Nitrate Salts Of Sodium And Potassium At 110 - 150°C

FY05 SUMMARY REPORT

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Abstract

Alloy 22 (a nickel-chromium-molybdenum-tungsten alloy) is being investigated for use as the outer barrier of waste containers for a high-level nuclear waste repository in the thick unsaturated zone at Yucca Mountain, Nevada. Experiments were conducted to assess crevice corrosion of Alloy 22 in de-aerated aqueous solutions of chloride and nitrate salts of potassium and sodium in the temperature range 110-150°C (some limited testing was also conducted at 90°C). Electrochemical tests were run in neutral salt solutions without acid addition and others were run in salt solutions with an initial hydrogen ion concentration of 10^{-4} molal. The Alloy 22 specimens were weld prism specimens and de-aeration was performed with nitrogen gas. No evidence of crevice corrosion was observed in the range 125-150°C.

In the 120 to 160°C temperature range, the anionic concentration of stable aqueous solutions is dominated by nitrate relative to chloride. At nominally 120°C, the minimum nitrate to chloride ratio is about 4.5, and it increases to about 22 at nominally 155°C. The absence of localized corrosion susceptibility in these solutions is attributed to the known inhibiting effect of the nitrate anion. At 110°C, aqueous solutions can have dissolved chloride in excess of nitrate. Localized corrosion was observed at nitrate to chloride ratios up to 1.0, the highest ratio tested. The extent of localized corrosion was confined to the crevice region of the samples, and was limited for nitrate to chloride ratios greater than or equal to 0.3.

Aqueous solution chemistry studies indicate that nitrate to chloride ratios of less than 0.5 are possible for temperatures up to nominally 116°C. However, the exact upper temperature limit is unknown and no electrochemical testing was done at these temperatures. Limited comparison between 8 m Cl aqueous solutions of Na + K on the one hand and Ca on the other indicated similar electrochemical E_{crit} values and similar morphology of attack, again limited to the crevice region. However, the 24 hr E_{corr} value was higher for the Ca based solution; this is probably due to the higher acidity of this solution (Ca^{2+} is slightly hydrolyzing). Intermediate-term corrosion potential (E_{corr}) measurements indicate that moderately acidic conditions are required to achieve elevated E_{corr} values.

1. Introduction

This report addresses possible crevice corrosion that might occur on the waste package outer barrier (comprised of Alloy 22) in a high-level waste repository in the thick unsaturated zone at Yucca Mountain, Nevada. In this non-pressurized environment, aqueous solutions may form and stably exist above the nominal boiling point of water due to high salt content (e.g., BSC 2004). The majority of the aqueous solutions that are predicted to form on the waste packages due to dust deliquescence consists of chloride and nitrate salts of sodium and potassium. Recent work indicates that deliquescence of

these salt mixtures can occur at temperatures in excess of 180°C [Rard 2004; Carroll et al 2005b]. Hence, understanding the degradation of Alloy 22 in these environments is necessary for the long-term prediction of waste package integrity.

Previous studies have shown that nitrate is an effective inhibitor of localized corrosion of corrosion resistant metal alloys [e.g. Brossia and Kelly 1998, Ilevbare et al. 2005]. This has been demonstrated for Alloy 22 in the temperature range 60 to 100°C for aqueous solutions of 1, 3.5 and 6 molal Cl [Ilevbare et al. 2005]. In the Ilevbare et al. study, localized corrosion inhibition was observed at 60°C with nitrate to chloride ratio of 0.15 and at 100°C with a ratio of 0.5

Aqueous solution characteristics

Carroll et al. [2005b] showed deliquescence of the NaCl + NaNO₃ + KNO₃ solids mixture occurring at temperatures up to at least 180°C. Carroll et al. [2005a] measured a maximum boiling point (BP) of 135°C for the saturated NaCl + KNO₃ aqueous solution. BPs were also determined for non-saturated solutions (and similar data were also collected in the present study.) In addition, Carroll et al. [2005a] measured a maximum BP of 155°C for an equimolar mixture of nearly saturated NaNO₃ + KNO₃ aqueous salt solution and a maximum BP in excess of 180°C for the saturated NaCl + NaNO₃ + KNO₃ salt solution.

Aqueous solution composition dependence on fixed relative humidity (RH) for the NaCl + KNO₃ system was obtained by Carroll et al. [2005a] at 90 and 120°C. At 90°C chloride-only (i.e., no nitrate) solutions are possible, however at 120°C stable chloride solutions must also contain nitrate. The minimum nitrate to chloride ratio occurs at the maximum RH (which depends on the temperature and the total pressure). This ratio at 120°C is approximately 3, with NO₃ and Cl concentrations at 19 and 6 molal, respectively.

More recently Carroll et al. [2005b] have investigated the aqueous solution composition dependence on RH for the NaCl + KNO₃ + NaNO₃ aqueous salt mixture at 120°C. For this system, the minimum nitrate to chloride ratio occurs at a measured RH of nominally 50% and is approximately equal to 5 with NO₃ and Cl concentrations at 25 and 5 molal, respectively.

This present work builds on these previous studies and obtains composition characteristics of aqueous solutions of nitrate and chloride salts of potassium and sodium in the temperature range 110 to 160°C. In particular, the focus of these studies is to determine the maximum amount of chloride that is soluble in these high temperature solutions because of known aggressiveness of chloride for inducing localized corrosion. Subsequent corrosion studies are conducted in test solutions based on these aqueous solution chemistry studies.

Corrosion

Corrosion studies have shown that nitrate is an effective inhibitor of localized corrosion of corrosion resistant metal alloys [Brossia and Kelly 1998, Ilevbare et al. 2005]. LLNL has shown that nitrate is an effective inhibitor of chloride induced localized corrosion of Alloy 22 in the temperature range 60 – 100°C and for concentrations of 1, 3.5 and 6 molal Cl [Ilevbare et al. 2005]. Localized corrosion inhibition was observed at 60°C with nitrate to chloride ratio of 0.15 and at 100°C with a ratio of 0.5.

Previous studies have indicated that nitrate ions can significantly increase the open circuit potential (E_{corr} , corrosion potential) of Alloy 22. The nitrate containing aqueous conditions that lead to elevated E_{corr} are temperatures greater than 120°C and moderately acidic conditions (< pH 3). In addition, the nitrate to chloride ratio in the aqueous solutions may also have an effect on E_{corr} , with higher ratios typically resulting in higher E_{corr} values.

2. Technical Approach and Methods

2.1. Aqueous Solution Composition Determination; Chloride and Nitrate Solubility Limits

In the present work, aqueous solution compositions in the temperature range 110 to 160°C were determined for solutions of NaCl, KCl, NaNO₃, and KNO₃. For solutions where chloride can dominate the solution composition, maximum nitrate solubility in a solution of a fixed chloride concentration was determined. These solutions are limited to temperatures less than about 116°C because of the temperature stability limitations of chloride dominated solutions. For solutions in which nitrate dominates the solutions, the maximum amount of soluble chloride was determined. These solutions can exist at much higher temperatures because of the very high boiling points of the mixed nitrate salt solutions. Solution compositions are limited to those containing sodium and potassium as cations, since the majority of predicted aqueous solution compositions on the waste packages from seepage and dust deliquescence do not contain significant amounts of calcium or magnesium cations.

Literature data indicates that for mixtures of NaCl and KCl the maximum chloride solubility occurs for nearly equimolar solutions (see green highlighted rows in Table 1) [Linke 1965 p. 147]. It is assumed that this relationship also holds in aqueous solutions of nitrate and chloride, that is, maximum chloride concentrations occur in solutions where sodium and potassium cations are equal in molar concentration. No experimental verification of this assumption in nitrate containing solutions was performed.

Equimolar KNO₃ and NaNO₃ aqueous solutions are used extrapolating the assumption that maximum anion concentrations can be obtained in solutions of equimolar Na + K, as was the case for chloride (see Table 1). No verification of this assumption for chloride in

nitrate dominated solutions was performed, however literature data does indicate that near maximum anion concentration in nitrate only solutions for equimolar K + Na [see Linke 1965 p. 263].

In addition, Carroll et al. [2005a] demonstrated that a saturated aqueous solution with equal parts of potassium and sodium nitrate had a boiling point near the maximum for the Na-K-NO₃-Cl system. Hence using equimolar nitrate solutions facilitates investigating solution composition characteristics for a large range of temperatures.

Table 1. Chloride solubility in aqueous salt solution of NaCl and KCl at 100°C. [Linke 1965 p. 147].

gms/100 gms saturated solution		molal			
KCl	NaCl	KCl	NaCl	Solids	Total Cl molal
35.69	0	7.44	0.00	KCl	7.44
30.4	6.3	6.44	1.70	KCl	8.14
29.95	6.48	6.32	1.74	KCl	8.06
27.7	9.43	5.91	2.57	KCl	8.48
25	12.5	5.36	3.42	KCl	8.79
24.88	12.69	5.35	3.48	KCl	8.82
22.4	15.5	4.84	4.27	KCl	9.11
22.2	15.9	4.81	4.40	KCl + NaCl	9.21
21.68	16.9	4.73	4.71	KCl + NaCl	9.44
19.12	18.12	4.09	4.94	NaCl	9.03
19	17.7	4.03	4.78	NaCl	8.81
10.25	22.57	2.05	5.75	NaCl	7.80
0	28	0.00	6.65	NaCl	6.65

It is acknowledged that the present study is not a thorough investigation of aqueous solutions of NaCl, KCl, NaNO₃, and KNO₃ in the temperature range 110 to 160°C. However, the intent of the investigation was to determine near-maximum amounts of chlorides that are soluble in high temperature nitrate dominated solutions and based on literature data, that is thought to occur in solutions with equimolar amounts of Na and K.

Methodology

Two approaches were taken to determine solubility limitations.

- A base chloride solution was made of equimolar NaCl and KCl. Then dry salts equivalent to 0.5 molal increments of KNO₃ and NaNO₃ were added in an alternating order. The additions were continued until the solubility limit was reached.
- A base nitrate solution was prepared of equimolar NaNO₃ and KNO₃. Then dry salts equivalent to 0.5 molal increments amounts of KCl and NaCl were added in an alternating order. The additions were continued until the solubility limit was reached.

The concentration of added salt was determined from the weight of the salt, molecular weight of the salts and the initial weight of water in the test cell. Because of the very strong temperature dependence of the nitrate salt solubility, the initial test solutions were made at elevated temperatures. Then incremental amounts of salt were added with a concurrent temperature elevation until the desired composition was reached.

To ensure that the maximum solubility was obtained in the chloride nitrate mixtures, the solutions were typically kept within approximately 4°C of their boiling point, which was measured after the addition of salt. After each addition of salt, the solution was kept near its boiling temperature until all the salt had dissolved. If the salt did not fully dissolve after several hours, the salt concentration just before the last addition was noted as the effective solubility limit.

A solution was also prepared to find the maximum solubility in a nitrate only solution (KNO_3 and NaNO_3). This test was started at 100 molal total nitrate, and 1 molal equivalents of dry salts of nitrates were incrementally added until the nitrates could no longer dissolve into the solution. The boiling point of this solution was measured. Similarly, the boiling point of a saturated solution of equimolar KCl and NaCl was also determined.

Test Apparatus

Solutions were placed in one-liter glass cells inside a heating mantle that was deep enough that the level of solution was completely inside the heater (to help minimize salt precipitation at the gas-solution interface). Water losses were reduced with a condenser that was cooled by water at nominally 8°C. The thermocouple was connected to a control unit that set and monitored the desired temperature. A nitrogen bubbling tube was extended into the solution and the flow of gas was kept at around 100 cm^3/min in order to mix the solution and to maintain slightly elevated pressure inside the vessel so as to minimize back diffusion of laboratory air. Figure 1 is a picture of the test apparatus.

Figure 1. Experimental setup for aqueous solution chemistry testing.

2.2. Corrosion Potential, E_{corr} (Open Circuit Potential)

The following electrochemical tests related to E_{corr} were performed:

- monitoring of corrosion potential E_{corr} evolution as a function of time
- polarization resistance measurements during E_{corr} evolution
- electrochemical impedance spectroscopy during E_{corr} evolution.

A three-electrode technique was used to conduct the electrochemical tests in a Pyrex corrosion cell containing a working electrode, an auxiliary electrode, and a Luggin capillary connected to a suitable reference electrode (Ag/AgCl or Hg/Hg₂Cl₂). Carbon dioxide scrubbed air was purged through a dispenser immersed in the solution, applying a controlled flow. A condenser was used to avoid excessive losses of fluid due to evaporation of test solution. Also, a special designed water-jacketed Luggin probe maintained the reference electrode at or near room temperature. A controlled-temperature, heating mantle was used to maintain the test temperature at the desired value. Specimens were cleaned sequentially with distilled water, hexane, acetone, and methanol (or ethanol) prior to testing or as otherwise noted. Monitoring of the test specimen corrosion potential, E_{corr} , was performed using Gamry potentiostats controlled by Gamry Framework Software.

The following ASTM procedures were used as guidelines for performing the electrochemical testing.

ASTM G 5 Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements

ASTM G 48 Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution

ASTM G 59 Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements

ASTM G 106 Standard Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements

In addition to monitoring the E_{corr} evolution with time, polarization resistance was performed periodically in order to obtain instantaneous corrosion (dissolution) rates, and electrochemical impedance spectroscopy (EIS) was performed in order to characterize the evolving oxide film. Obtaining these three complementary parameters should give a good indication of when the E_{corr} values have obtained steady state for a particular set of environmental conditions.

Non-welded Alloy 22 prism specimens were used in this testing. The creviced area on the specimens was minimal; limited to the mounting rod washer. Carbon dioxide scrubbed laboratory air was bubbled through the test solutions. The CO₂ was removed from the air

in order to keep steady-state hydrogen ion concentrations; the CO₂ level in the laboratory air is not controlled or monitored. The acid test solutions were included in order to investigate conditions where E_{corr} is expected to obtain elevated values. The oxidizing effect of nitrate is accelerated at low pH. Solutions designated as neutral are those with no acid addition and purge gas is carbon dioxide scrubbed air.

Only a very limited number of tests were performed at under very acidic conditions because of health and safety concerns with acid gas volatility. Methods to remove the acid gases that evolve during set up and testing are presently being investigated.

2.3. E_{crit} Determination; Chloride + Nitrate solutions; 110°C to 150°C

The electrochemical cyclic potentiodynamic polarization (CPP) procedure was used to determine E_{crit} values. CPP electrochemical tests were used to identify the breakdown potentials, the potential at which passivity is lost on the forward scan, and the crevice repassivation potentials, the potential below which localized corrosion initiation susceptibility is considered unlikely. The breakdown potential is reported as E20, the potential on the forward scan at which the anodic current density reaches 20×10^{-6} amps/cm². The repassivation potential is reported as the potential (ER1) at which the current density is about 1 $\mu\text{A}/\text{cm}^2$ on the reverse scan.

Cyclic potentiodynamic polarization (CPP) is a standard electrochemical procedure for determining electrochemical parameters relevant to corrosion. Several ASTM procedures listed are used as guidelines. The CPP testing was performed with the Gamry potentiostat and controlled with Gamry Framework Software.

A limited number of potentiostatic tests were also performed as confirmation that crevice initiation can occur at potentials near the repassivation potential. Potentiostatic testing was performed at potentials above the crevice repassivation potential as determined from the CPP. The ER1 potentials, as defined above, were used as the crevice repassivation potential.

Test Apparatus

A three-electrode technique was used to conduct the electrochemical tests in a Pyrex corrosion cell which contained a working electrode (prism crevice assembly), graphite counter or platinum electrode, and a Luggin capillary connected to a suitable reference electrode (Ag/AgCl or Hg/Hg₂Cl₂). Inert gas was purged through a dispenser immersed in the solution with a controlled flow. A condenser was used to avoid excessive evaporation of test solution. Also, a special designed water-jacketed Luggin probe maintained the reference electrode at or near room temperature. After polishing, specimens were cleaned sequentially with distilled water, hexane, acetone, and methanol (or ethanol) prior to testing or as otherwise noted in test data sheets. A controlled temperature heating mantle was used to maintain the test temperature at the desired value.

The following ASTM procedures were used as guidelines for performing the electrochemical testing.

ASTM G 5 Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements

ASTM G 48 Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution

ASTM G 59 Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements

ASTM G 61 Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys

ASTM G 106 Standard Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements

Post-test cleaning was performed as appropriate, as determined by specimen examination. The post-test specimens were initially examined visually, then by microscopic evaluation to detect the presence or absence of localized corrosion.

As with the measurement of E_{corr} , aqueous solutions are limited to those obtainable using salts containing sodium (Na) and potassium (K), and not salts of calcium (Ca) and magnesium (Mg). These electrochemical tests were run in de-aerated solutions using nitrogen gas as the purge gas.

Several tests were to have been performed in autoclaves. The use of autoclaves was necessary for a number of reasons, such as the boiling points of the test solutions are exceeded at normal atmospheric pressure or the solution composition is near the solubility limit at the test temperature. These tests were to be performed in order to extend the E_{crit} determination to the limits of stability (boiling point under atmospheric pressure) of the solution composition. (Tests at or near boiling conditions are experimentally difficult to perform, hence, the use of an autoclave simplifies the testing). The electrochemical autoclaves were ordered soon after funding for these studies became available. Unfortunately, autoclaves were not delivered until late September 2005 and there were several safety issues with the autoclaves in the as-delivered condition.

3. Results and Discussion

3.1. Aqueous solution chemistry

The aqueous solution chemistry studies were as follows:

- For temperatures greater than 120°C, the focus was to determine the maximum concentration of chloride for a given nitrate concentration, with the concurrent determination of the corresponding boiling point.
- For temperatures less than 116°C, the focus was to determine the maximum concentration of nitrate for a given chloride concentration, again with the concurrent determination of the corresponding boiling point.
- The maximum solubility of chloride-only and nitrate-only solutions were also determined, along with the associated boiling points

Tables 2 and 3 list the parameters that were used in the testing. Tables 4 and 5 list the test results. The methodology of obtaining the uncertainties of the points in Figures 2-6 is described in Appendix A. The results of the uncertainty calculations are also listed there.

Table 2. Test parameters for determination of chloride solubility in nitrate solutions.

Nitrate molality	Initial Salt (g)		Initial DI water (g)	Increment (g) equal to 0.5 molal Cl^-	
	KNO_3	NaNO_3		KCl	NaCl
25	379.2	318.7	300	11.1	8.7
42	530.8	446.2	250	9.3	7.3
50	631.9	531.2	250	9.3	7.3
75	568.7	478.1	150	5.6	4.4
85	644.6	541.8	150	5.6	4.4
100	606.7	509.9	120	4.5	3.5

Table 3. Test parameters for determination of nitrate solubility in chloride solutions.

Chloride molality	Initial Salt (g)		Initial DI water (g)	Increment (g) equal to 0.5 molal NO_3^-	
	KCl	NaCl		KNO_3	NaNO_3
6	89.5	70.1	400	20.2	17.0
8	119.3	93.5	400	20.2	17.0
9	167.8	131.5	500	25.3	21.2

Table 4. Boiling points of nitrate chloride solutions. Nitrate fixed and chloride variable. [DTN LL051100623121.054].

		Boiling Points (°C)										
		Chloride molality										
		0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
Nitrate molality	25	118.7		119.9		120.3		121.8		121.8		122.3
	42			128.0								
	50	131.3		133.1		133.0		134.9		134.7		
	75	141.3		141.7	142.3	142.3	142.8	144.7	145.2	145.2		
	85	145.0				146.8	149.7	147.3		147.1	148.0	
	100	150.5	150.2	152.4	154.5	155.2	156.3	155.2	158.3	160.3	160.9	
	111	154.9										
	30	121.2										
	45	129.5										
	60	136.4										
	67.5	139.1										
	75	143.6										
	90	151.8										

Table 5. Boiling points of nitrate chloride solutions. Chloride fixed and nitrate variable. [DTN LL051100623121.054].

		Boiling Points (°C)			
		Nitrate molality			
		0	3	6	18
Chloride molality	6				115.0
	8			116.5	
	9	111.6	115.0		

In Figure 2, the solubility limit of chloride (in terms of molality) is plotted as a function of the molality of nitrates. Note that this is not an isothermal plot; the temperature increases along the x-axis. At lower nitrate concentration, chloride salt solubility decreases with increasing nitrate. However, for solutions with nitrate concentrations exceeding 50 molal, the amount of chloride able to dissolve became nearly constant and may have slightly increased in the most concentrated nitrate solutions. Unfortunately the experimental error at the highest concentrations also increased, and more testing would be required to determine if this trend was real or not. However, it was clear that the maximum chloride concentration was at least leveling off at the highest nitrate concentrations. Solution temperatures were above 140°C for these high nitrate compositions as can be seen in Figure 3.

The boiling points for the salt mixtures are functions of both nitrate and chloride concentrations and are plotted in Figure 3. The boiling point temperatures increased linearly with rising nitrate levels. At the higher nitrate concentrations, relatively small amounts of chloride can significantly elevate the solution boiling point; however, the extent of the boiling point elevation induced by chloride is limited by chloride solubility in these solutions.

Figure 2. Maximum chloride concentration in nitrate aqueous solutions

Figure 3. Boiling point temperatures for chloride-nitrate aqueous solutions. For nitrate concentrations greater than 20 molal, boiling points were measured to the chloride solubility limit for fixed nitrate solutions. For nitrate molalities less than 20 molal, boiling points were measured to the nitrate solubility limited for fixed chloride solutions except for the chloride only solution (i.e. 0 m NO₃). Only integer increments of chloride molality are plotted.

The relative humidity of the solutions at the maximum solubility was calculated from water vapor pressure [Weast and Astle 1981] at the boiling point temperatures of the solutions. Relative humidity is calculated as the ratio of the vapor pressure of the test solution (one atmosphere at boiling) divided by the vapor pressure of pure water at the same temperature.

This relative humidity is plotted as a function of chloride mole fraction (Figure 4). It is assumed that these points mark the phase diagram boundary that separates the liquid phase only region from the liquid + solid-chloride region. The points at zero mole fraction on the abscissa of the figure are for pure nitrate solutions.

Although the plot is a simplification (due to the inclusion of multiple temperature data) it is believed that this plot allows insight into whether or not these solutions provide a maximum chloride to nitrate ratio for a given relative humidity. The steepness of the phase boundary for RH less than 0.4 indicates that near minimum values of nitrate to

chloride ratios are obtained using the experimental data in this region. However, above 0.4 RH, direct measurement of chloride solubility for a given nitrate concentration is needed in order to ensure testing at the minimum nitrate to chloride ratio. In terms of temperature, the concern about obtaining the maximum chloride in the solution composition applies primarily to the results obtained at temperatures less than about 120°C.

Figure 4. The phase boundary for chloride nitrate mixtures. This is not a typical phase diagram of similar appearance as this diagram includes data from several different temperatures.

Boiling points were obtained for equimolar KNO_3 and NaNO_3 solutions (see Figure 5). Included in the figure is the boiling point for the mutually saturated solution. All the points lie with a high level of precision along a linear trend. The highest boiling point measured here agrees well with that measured previously by Carroll et al.[2005a].

Figure 5. Measured boiling points for equimolar KNO_3 and NaNO_3 aqueous solutions. Note: That the calculated solution composition of 111 m NO_3 assumes that the starting solution contained 100 m NO_3 because it boiled at 150°C , similar to another 100 m NO_3 solution in this study. However, entries in the scientific notebook for this solution indicate a slightly lower concentration because a 100 g addition of NaNO_3 was not entered. It is assumed that the omission was inadvertent.

Nitrate to chloride ratios are important for corrosion applications because nitrate tends to reduce the aggressiveness of chloride as noted previously. Figure 6 shows the minimum NO_3/Cl ratio for four-salt (KNO_3 , NaNO_3 , KCl , NaCl) solutions as a function of boiling point temperature. These solutions contain the maximum amount of chloride for a given nitrate concentration at the boiling point. The results are important because they indicate that solutions with low NO_3/Cl ratios are not possible at higher temperatures. Indeed ratios near 0.5 would require temperatures of 115°C or lower. Note: The four-salt KNO_3 - NaNO_3 - KCl - NaCl system is factually the same as the “three-salt” KNO_3 - NaNO_3 - NaCl system, as KCl solid will spontaneously form from KNO_3 and NaCl in this temperature range (cf. BSC 2004, Section 6.7.2.9). KCl also forms in the “two-salt” system KNO_3 - NaCl in this temperature range (without forming solid NaNO_3).

Figure 6. Minimum Nitrate to Chloride ratios for four-salt (KNO_3 , NaNO_3 , KCl , NaCl) solutions with boiling temperatures above 115°C

Comparison with previous studies

Minimum NO_3 to Cl ratios derived from solubility data from deliquescence testing agree well with the data in Figure 6. From data on a salt mixture of $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3$ at 120°C the measured solubility data give a minimum NO_3 to Cl ratio that is about 5 [Carroll et al 2005b]. And from data on a salt mixture of $\text{NaCl} + \text{KNO}_3$ at 120°C the measured solubility data give a minimum NO_3 to Cl ratio that is about 3 [Carroll et al 2005a]. From Figure 6, the interpolated minimum nitrate to chloride ratio is approximately 3.

3.2. E_{corr} evolution monitoring

The dependence of E_{corr} on the aqueous solution acidity level is shown in Figure 7. The results are for a 25m $\text{NO}_3 + 1\text{m Cl}$ aqueous solution at 110°C . These results indicate a strong increase in E_{corr} when the $\log(\text{H}^+ \text{ molality})$ (subsequently referred to as “pH”) decreases from 3 to 2. The steady state E_{corr} values at $\log(\text{H}^+ \text{ molality}) = 2$ is very near the redox potentials for the following couples [Pourbaix 1974]: $\text{NO}_3\text{-NO}_2$ and $\text{NO}_3\text{-NH}_4$.

The E_{corr} values for the lower acidity solutions are far from these values, although there is a steady increase in E_{corr} values with increasing acidity. The increase in E_{corr} with

increasing acidity is consistent with the known effect of nitrate becoming more oxidizing under more acidic conditions.

Figure 7. Effect of acidity on Alloy 22 prism open circuit potentials; $[\text{NO}_3] / [\text{Cl}] = 25:1$, 110°C [DTN LL051001312251.155].

3.3. E_{crit} determination with cyclic potentiodynamic polarization

The results of the cyclic potentiodynamic polarization (CPP) testing are listed in Table 6. The breakdown potential is reported as E_{20} , and the repassivation potential as E_{R1} . Also reported in the table is whether localized corrosion occurred or not. Optical microscopy was used to examine the surfaces to assess the occurrence of localized corrosion. Localized corrosion was not observed for temperatures greater than 125°C . At 110°C , localized corrosion was observed at nitrate to chloride ratios up to 1, the highest ratio tested. The extent of localized corrosion was confined to the crevice region, and was limited for ratios greater than or equal to 0.3.

Table 6. Summary of E_{crit} determination studies including solution composition & temperature, and occurrence of localized corrosion as determined by optical microscopy. DTN: LL051001012251.154.

Sample ID	Temp (°C)	log(H ⁺ molality)	Cl (molal)	NO ₃ (molal)	NO ₃ /Cl	Localized Corrosion (Yes/No)	E _{corr} (24hr) (V, Ag/AgCl)	E ₂₀ (V, Ag/AgCl)	E _{R1} (V, Ag/AgCl)	Notes
Cyclic Polarization Tests:										
KE0592	90	neutral	8	0.8	0.1	Yes	-0.12	0.727	0.570	
KE0688B	90	neutral	8	0.8	0.1	Yes	-0.501	0.683	-0.063	Re-use specimen
KE0590	90	neutral	8	1.6	0.2	Yes	-0.485	0.694	0.401	
KE0693B	90	neutral	8	1.6	0.2	Yes	-0.491	0.687	0.382	Re-use specimen
KE0588	110	Not determined	8	0	0	Yes	-0.321	0.035	-0.180	4m CaCl ₂
KE0689	110	neutral	8	0	0	Yes	-0.557	0.085	-0.200	
KE0691	110	neutral	8	0	0	Yes	-0.555	0.048	-0.182	
KE0687	110	neutral	8	0.8	0.1	Yes	-0.521	0.360	-0.047	
KE0692	110	neutral	8	0.8	0.1	Yes	-0.397	0.552	-0.096	
KE0589	110	neutral	8	1.6	0.2	Yes	-0.528	0.466	-0.017	
KE0591	110	neutral	8	2.4	0.3	Yes	-0.558	0.587	0.320	Slight localized corrosion under the crevice.
KE0580	110	neutral	8	4	0.5	Yes	-0.521	0.620	0.328	Slight localized corrosion under the crevice.
KE0690	110	neutral	6	6	1	Yes	-0.543	0.600	0.383	Slight localized corrosion under the crevice.
KE0581	110	neutral	6	6	1	Yes	0.216	0.684	0.522	Slight localized corrosion under the crevice.
KE0574	110	4	8	0	0	Yes	-0.412	0.049	-0.207	
KE0573	110	4	8	0.8	0.1	Yes	-0.376	0.508	-0.097	
KE0572	110	4	8	4	0.5	Yes	-0.303	0.668	0.443	Slight localized corrosion under the crevice.
KE0571	110	4	6	6	1	Yes	0.195	0.650	0.444	Slight localized corrosion under the crevice.
KE0575	110	4	6	6	1	Yes	-0.406	0.684	0.480	Slight localized corrosion under the crevice.
KE0695	110	neutral	2	42	21	No	-0.232	0.828	0.674	
KE0696	110	neutral	1	42	42	No	-0.427	0.846	0.690	
KE0280	110	neutral	0	42	N/A	No	-0.360	0.855	0.773	
KE0582	110	4	4	42	10.5	No	-0.108	0.779	0.654	
KE0583	110	4	2	42	21	No	-0.297	0.816	0.661	
KE0584	110	4	1	42	42	No	-0.323	0.829	0.661	
KE0697	125	neutral	4	42	10.5	No	-0.438	0.777	0.622	
KE0698	125	neutral	4	42	10.5	No	-0.471	0.780	0.683	
KE0586	125	neutral	2	42	21	No	-0.202	0.749	0.595	
KE0686	125	neutral	1	42	42	No	-0.528	0.749	0.608	

KE0281	125	neutral	0	42	N/A	No	-0.412	0.781	0.685	
KE0585	125	4	4	42	10.5	No	-0.234	0.743	0.540	
KE0587	125	4	2	42	21	No	-0.406	0.765	0.590	
KE0576	125	4	1	42	42	No	-0.242	0.785	0.685	
KE0578	140	4	1	72	72	No	-0.351	0.790	0.640	
KE0577	140	neutral	1	72	72	No	-0.383	0.820	0.725	
KE0699	140	neutral	3	76	25.3	No	-0.13	0.783	0.623	
KE0700	140	neutral	3	76	25.3	No	-0.418	0.785	0.656	
KE0595	150	neutral	1	100	100	No	-0.334	0.785	0.671	
Potentiostatic Tests:										
KE0593	110	neutral	8	0.8	0.1	Yes	E _{app} = 0.05 V. Severe attack with no stifling observed			
KE0594	110	neutral	8	1.6	0.2	Yes	E _{app} = 0.05 V. Severe attack with no stifling observed			

Figures 8 and 9 are plots of the E20 and ER1 dependence on NO₃/Cl ratio. These plots graphically illustrate that there is no discernable difference in E20 and ER1 values for NO₃ to Cl ratios greater than about 10. No localized corrosion was observed for these values. For ratios between 0 and 10 there is a steady increase in both ER1 and E20. Localized corrosion observed up to a ratio of 1.

Figure 8. E20 and ER1 as a function of NO₃ to Cl ratio.

Figure 9. E20 and ER1 as a function of NO_3^- to Cl ratio.

Figures 10 and 11 are illustrative examples of the electrochemical results for which no localized corrosion occurred and for which localized corrosion occurred.

Figure 10. CPP curve showing no localized corrosion. DTN: LL050906112251.152

Figure 11. CPP curve showing localized corrosion. DTN: LL050906112251.152

Figures 12-17 are optical images of the specimens tested at 110°C illustrating the decreasing extent of localized corrosion with increasing NO₃/Cl ratios. As illustrated the localized corrosion that did occur was confined to the region underneath the crevice former.

Figure 12. After CPP test in 8m $[\text{Cl}^-]$ + 4m $[\text{NO}_3^-]$ solution, $[\text{NO}_3^-]/[\text{Cl}^-]$ of 0.5:1, and 110°C. Limited crevice corrosion was observed optically. Specimen ID # KE0580.

Figure 13. After CPP test in 6m $[\text{Cl}^-]$ + 6m $[\text{NO}_3^-]$ solution, $[\text{NO}_3^-]/[\text{Cl}^-]$ of 1:1, and 110°C. Limited crevice corrosion was observed optically. Specimen ID # KE0581.

Figure 14. After CPP test in 8m $[\text{Cl}^-]$ + 0.8m $[\text{NO}_3^-]$ solution, $[\text{NO}_3^-]/[\text{Cl}^-]$ of 0.1:1, and 110°C. Crevice corrosion was observed optically. Specimen ID # KE0587.

Figure 15. After cyclic Polarization measurement in 8m $[\text{Cl}^-]$ solution, $[\text{NO}_3^-]/[\text{Cl}^-]$ of 0:1, and 110°C. Crevice corrosion was observed optically. Specimen ID # KE0689

Figure 16. After CPP test in 1m $[\text{Cl}^-]$ + 72m $[\text{NO}_3^-]$ solution, $[\text{NO}_3^-]/[\text{Cl}^-]$ of 72:1, and 140°C. No crevice corrosion was observed optically. Specimen ID#KE0578

Comparison with previous studies

In order to compare the effect of the solution cation on localized corrosion susceptibility of Alloy 22, a CPP test was run in an 8 m Cl^- solution formulated with CaCl_2 and at 110°C . The CPP curve is shown in Figure 17. The CPP curves for 8 m Cl^- solution formulated with $\text{NaCl} + \text{KCl}$ are shown for comparison. The data indicates similar electrochemical E_{crit} values. Similar morphology of attack – limited to crevice region – was also seen. However, the 24 hr E_{corr} value was higher for the calcium based solution; this is probably due to the more acidic calcium based solution.

The morphology of attack for this calcium based test is different than those that have been noted previously. In the previous studies massive attack occurred outside of the crevice region. This could be do to the much higher chloride contents used in those studies and the higher “turn around current” used for reversing the CPP scan.

The data presented in this report are also consistent with previously obtained data for sodium based chloride and nitrate solutions. Those tests likewise showed that nitrate inhibition of localized corrosion of Alloy 22 in the temperature range 60 to 100°C increases with increasing nitrate to chloride ratio. No localized corrosion was observed for the ratio of 0.5 at 100°C and at 0.15 at 60°C . These results combined with the present study suggest that in addition to nitrate to chloride ratio that temperature and absolute chloride and nitrate levels may affect localized corrosion susceptibility.

Figure 17. CPP curves for 8 m Cl test solutions. LL050906112251.152

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LL050904812251.151. Effect of pH on Corrosion Potential of Alloy 22 Prism Samples; Nitrate to Chloride Ratio of 25:1 110 Degrees C. Submittal date: 10/26/2005.

LL050906112251.152. Electrochemical Polarization Measurements of Alloy 22 in High Concentrated Brines at Temperatures from 90 to 150 Degrees Celsius. Submittal date: 10/11/2005.

LL051001012251.154. Localized Corrosion Susceptibility of Alloy 22 in High Concentrated Brines at Temperatures from 90 to 150 Degrees Celsius. Submittal date: 10/11/2005.

LL051001312251.155. Excel Table and Plot Displaying the Effect of pH on Corrosion Potential of Alloy 22 Prism Samples; Nitrate to Chloride Ratio of 25:1, 110 Degrees C. Submittal date: 10/31/2005.

LL051100623121.054 Na-K-NO₃-Cl Aqueous Solution Compositions at 110 to 160C; Support to Electrochemical Studies.

Appendix A. Calculation of uncertainties for the aqueous solution chemistry studies.

This appendix describes the methodology used to calculate the uncertainty associated with the aqueous solution chemistry measurements. Uncertainties took into consideration both the smallest scale of the instrument along with an estimate of the testing apparatus' capacity to control the parameter.

Temperature - The resolution of the digital thermometers was 0.1°C, however the thermometers were only calibrated with a tolerance of 1.0°C. The readings were not always steady when boiling was observed so the uncertainty estimate was 1.5°C.

Mass H₂O - The relatively large water mass uncertainty (Δm_{H_2O}) is estimated as 10.0 g and is the result of considerations of experimental setup. Water losses could occur through the seals on the vessels and through the condenser. In addition water losses could occur during the high temperature addition of the salt through an open port. The latter loss was somewhat reduced by lowering the temperature of the test solution during the salt additions in order to reduce the water vapor pressure.

Salt Mass - The estimated salt mass uncertainty (e.g, Δm_{Cl}) is also due to considerations of the experimental set-up. The analytical balance was calibrated with a tolerance of 0.1 g. Uncertainty was estimated to be 0.3 g because some non-dissolved salt would stick to the side of the vessel, and in addition, small amounts of salt precipitates formed near the nitrogen bubbler inlet. The latter effect was probably due to the solution cooling by the inlet nitrogen gas.

Calculation of uncertainties based on measurement uncertainty estimates

Uncertainty dependence on individual parameters was calculated as the relative uncertainty dependence on the particular parameter. For example, the total uncertainty in nitrate molality (Δm_{NO_3}) due to the measurement uncertainty in the amount of water is:

$$\Delta m_{NO_3} \text{ (water mass)} = m_{NO_3} * (\Delta m_{H_2O} / \text{total mass of } H_2O)$$

The total uncertainty of the nitrate molality is dependent on the uncertainty in the amount of water and the amount added nitrate, and is calculated as the square root of the sum the individual certainties squared.

$$\Delta m_{NO_3} \text{ (total)} = [(\Delta m_{NO_3} \text{ (water mass)})^2 + (\Delta m_{NO_3} \text{ (nitrate mass)})^2]^{0.5}$$

The uncertainty of the product of two parameters is calculated as the product of the sum of the relative uncertainties of the individual parameters and the product of the two parameters. For the nitrate to chloride ratio, this is:

$$\Delta(m_{NO_3} / m_{Cl}) = (m_{NO_3} / m_{Cl}) * (\Delta m_{NO_3} \text{ (total)} + \Delta m_{Cl} \text{ (total)}).$$

Table 7. Calculated uncertainties of NO₃ and Cl molality.

	NO ₃ (molal)	Max Cl (molal)	Solution composition					Uncertainty in NO ₃ molal H ₂ O (mass) dependence	Uncertainty in Cl molal H ₂ O (mass) dependence	Uncertainty in NO ₃ molal NO ₃ (mass) dependence	Uncertainty in Cl molal Cl (mass) dependence	Δm_{NO_3} (total) Total uncertainty in NO ₃ molal	Δm_{Cl} (total) Total uncertainty in Cl molal
			H ₂ O (kg)	KNO ₃ (g)	NaNO ₃ (g)	KCl (g)	NaCl (g)						
Fixed Cl solutions	0	9	0.5	0	0	167.8	131.5	0.0000	0.1800		0.0090		0.1802
	3	9	0.5	75.9	63.9	167.8	131.5	0.0600	0.1800	0.0064	0.0090	0.0603	0.1802
	6	8	0.4	121.2	102	119.3	93.5	0.1500	0.2000	0.0081	0.0113	0.1502	0.2003
	18	6	0.4	363.9	306	89.5	70.1	0.4500	0.1500	0.0081	0.0113	0.4501	0.1504
Fixed NO ₃ solutions	25	5.5	0.3	379.2	318.8	66.6	43.5	0.8333	0.1833	0.0107	0.0150	0.8334	0.1839
	42	4	0.25	530.8	446.2	37.2	29.2	1.6800	0.1600	0.0129	0.0181	1.6800	0.1610
	50	4	0.25	631.9	531.3	37.2	29.2	2.0000	0.1600	0.0129	0.0181	2.0000	0.1610
	75	3.5	0.15	568.7	478.1	22.4	13.2	5.0000	0.2333	0.0215	0.0295	5.0000	0.2352
	85	4.5	0.15	644.6	541.8	28	17.6	5.6667	0.3000	0.0215	0.0296	5.6667	0.3015
	100	4.5	0.12	606.7	509.9	22.5	14	8.3333	0.3750	0.0269	0.0370	8.3334	0.3768
NO ₃ only solutions	111*		0.12	673.8	566	0	0	9.2500	0.0000	0.0269		9.2500	
	30		0.2	303.3	255	0	0	1.5000	0.0000	0.0161		1.5001	
	45		0.2	455	382.5	0	0	2.2500	0.0000	0.0161		2.2501	
	60		0.2	606.7	509.9	0	0	3.0000	0.0000	0.0161		3.0000	
	67.5		0.2	758.4	509.9	0	0	3.3750	0.0000	0.0160		3.3750	
	75		0.2	758.4	637.4	0	0	3.7500	0.0000	0.0161		3.7500	
	90		0.2	910.1	764.9	0	0	4.5000	0.0000	0.0161		4.5000	

Table 8. Boiling point temperatures as a function of chloride and nitrate concentrations. Uncertainty of nitrate molality is listed and the uncertainty of temperature is fixed at 1.5°C.

	Boiling Points (°C)														
NO ₃ (molality)															Δm _{NO3} (total) Total uncertainty in NO ₃ molal
	Cl (molality)														
	0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	6	8	9	---
0														111.6	
3														115.0	0.0603
6													116.5		
18												115.0			0.4501
25	118.7		119.9		120.3		121.8		121.8		122.3				0.8334
42			128.0												1.6800
50	131.3		133.1		133.0		134.9		134.7						2.0000
75	141.3		141.7	142.3	142.3	142.8	144.7	145.2	145.2						5.0000
85	145.0				146.8	149.7	147.3		147.1	148.0					5.6667
100	150.5	150.2	152.4	154.5	155.2	156.3	155.2	158.3	160.3	160.9					8.3334
111*	154.9														9.2500
30	121.2														1.5001
45	129.5														2.2501
60	136.4														3.0000
67.5	139.1														3.3750
75	143.6														3.7500
90	151.8														4.5000

* Note: That the calculated solution composition of 111 m NO₃ assumes that the starting solution contained 100 m NO₃ because it boiled at 150°C, similar to another 100 m NO₃ solution in this study. However, entries in the scientific notebook for this solution indicate a slightly lower concentration because a 100 g addition of NaNO₃ was not entered. It is assumed that the omission was inadvertent.

Table 9. Solution boiling point temperature dependence on total nitrate molal concentration with associated nitrate molal uncertainty. The uncertainty in the boiling point temperature is fixed at 1.5°C.

NO ₃ (molal)	Boiling point (°C)	Δm_{NO_3} (total) (total uncertainty in NO ₃ molal)
25	118.7	0.83
50	131.3	2.00
75	141.3	5.00
85	145	5.67
100	150.5	8.33
111*	154.9	9.25
30	121.2	1.50
45	129.5	2.25
60	136.4	3.00
67.5	139.1	3.38
75	143.6	3.75
90	151.8	4.50

* Note: That the calculated solution composition of 111 m NO₃ assumes that the starting solution contained 100 m NO₃ because it boiled at 150°C, similar to another 100 m NO₃ solution in this study. However, entries in the scientific notebook for this solution indicate a slightly lower concentration because a 100 g addition of NaNO₃ was not entered. It is assumed that the omission was inadvertent.

Table 10. Data for molal ratio of NO₃ to Cl as a function of boiling point temperature. Determination of uncertainty is discussed in the text.

NO ₃ (molality)	Max Cl (molality)	Boiling Point (°C)	NO ₃ (molality) / Cl (molality)	Δm_{NO_3} (total) Uncertainty in NO ₃ molality	Δm_{Cl} (total) Uncertainty in Cl molality	Uncertainty in NO ₃ /Cl
3	9	115	0.3	0.0603	0.1802	0.013
6	8	116.5	0.8	0.1502	0.2003	0.038
18	6	115	3.0	0.4501	0.1504	0.150
25	5.5	122.9	4.5	0.8334	0.1839	0.304
50	4	134.7	12.5	2.0000	0.1610	1.003
75	3.5	145.2	21.4	5.0000	0.2352	2.869
85	4.5	148	18.9	5.6667	0.3015	2.525
100	4.5	160.9	22.2	8.3334	0.3768	3.713

Table 11. Solubility limit for chloride in nitrate solutions with associated uncertainties in chloride and nitrate molal concentrations.

	NO ₃ (molal)	Max Cl (molal)	Soluti on compo sition					Uncertainty in NO ₃ molal H ₂ O (mass) dependence	Uncertainty in Cl molal H ₂ O (mass) dependence	Uncertainty in NO ₃ molal NO ₃ (mass) dependence	Uncertainty in Cl molal Cl (mass) dependence	Δm_{NO_3} (total) Total uncertainty in NO ₃ molal	Δm_{Cl} (total) Total uncertainty in Cl molal
			H ₂ O (kg)	KNO ₃ (g)	NaNO ₃ (g)	KCl (g)	NaCl (g)						
Fixed Cl solutions	0	9	0.5	0	0	167.8	131.5		0.1800		0.0090		0.1802
	3	9	0.5	75.9	63.9	167.8	131.5	0.0600	0.1800	0.0064	0.0090	0.0603	0.1802
	6	8	0.4	121.2	102	119.3	93.5	0.1500	0.2000	0.0081	0.0113	0.1502	0.2003
	18	6	0.4	363.9	306	89.5	70.1	0.4500	0.1500	0.0081	0.0113	0.4501	0.1504
Fixed NO ₃ solutions	25	5.5	0.3	379.2	318.8	66.6	43.5	0.8333	0.1833	0.0107	0.0150	0.8334	0.1839
	42	4	0.25	530.8	446.2	37.2	29.2	1.6800	0.1600	0.0129	0.0181	1.6800	0.1610
	50	4	0.25	631.9	531.3	37.2	29.2	2.0000	0.1600	0.0129	0.0181	2.0000	0.1610
	75	3.5	0.15	568.7	478.1	22.4	13.2	5.0000	0.2333	0.0215	0.0295	5.0000	0.2352
	85	4.5	0.15	644.6	541.8	28	17.6	5.6667	0.3000	0.0215	0.0296	5.6667	0.3015
	100	4.5	0.12	606.7	509.9	22.5	14	8.3333	0.3750	0.0269	0.0370	8.3334	0.3768
	111*		0.12	673.8	566	0	0	9.2500	0.0000	0.0269		9.2500	

* Note: That the calculated solution composition of 111 m NO₃ assumes that the starting solution contained 100 m NO₃ because it boiled at 150C, similar to another 100 m NO₃ solution in this study. However, entries in the scientific notebook for this solution indicate a slightly lower concentration because a 100 g addition of NaNO₃ was not entered. It is assumed that the omission was inadvertent.