Inconel 690 Corrosion in WTP HLW Glass Melts Rich in Aluminum, Bismuth, Chromium or Aluminum/Sodium

September 23, 2008

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Office of River Protection

P.O. Box 450
Richland, Washington 99352

Approved for Public Release;
Further Dissemination Unlimited

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VSL-08R1370-1

Final Report

**Inconel 690 Corrosion in WTP HLW Glass Melts Rich in Aluminum,
Bismuth, Chromium or Aluminum/Sodium**

prepared by

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and

**Department of Energy
Office of River Protection**

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The Catholic University of America*

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This report describes the results of testing specified by the above Test Plan. The work was performed in compliance with the quality assurance requirements specified in the Test Plan. Results required by the Test Plan are reported. The test results and this report have been reviewed for correctness, technical adequacy, completeness, and accuracy.

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Vitreous State Laboratory
The Catholic University of America

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List of Abbreviations

CUA	Catholic University of America
DCP-AES	Direct Current Plasma-Atomic Emission Spectroscopy
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
HLW	High Level Waste
IC	Ion Chromatography
LAW	Low Activity Waste
ORP	Office of River Protection
SEM-EDS	Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy
VSL	Vitreous State Laboratory
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WVDP	West Valley Demonstration Project
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

SECTION 1 INTRODUCTION

This report presents the results from work that was conducted to assess the corrosion of Inconel 690 in recently developed high waste loading High Level Waste (HLW) glass formulations at temperatures at, and somewhat above the nominal melter operating temperature planned for the Hanford Tank Waste Treatment and Immobilization Plant (WTP) HLW melters. This report is prepared in response to a statement of work supplied by the Department of Energy's (DOE) Office of River Protection (ORP) [1] and corresponding Test Plan [2].

ORP has estimated the number of high-level waste (HLW) canisters to be produced at the WTP at about 13,500 (equivalent to 40,500 MT glass) [1]. This estimate is based upon the inventory of the tank wastes, the anticipated performance of the sludge treatment processes, and current assumptions regarding the capability of the borosilicate glass waste form. Glass formulations with higher waste loadings have the potential to significantly reduce the projected number of canisters, which would lead to significant cost and schedule reductions. The baseline WTP HLW glass formulation efforts have been conservative in terms of achievable waste loadings. These formulations have been specified to ensure that the glasses are homogenous, contain essentially no crystalline phases, are processable at 1150°C in joule-heated, ceramic-lined melters, and meet WTP Contract requirements.

The overall mission of the WTP will require the immobilization of tank waste compositions that are dominated by mixtures of aluminum (Al), chromium (Cr), bismuth (Bi), iron (Fe), phosphorous (P), zirconium (Zr), and sulfur (S) compounds as waste-limiting components. Although the focus of the principal WTP research and technology work has been on the early HLW compositions, which are iron-limited, recently, DOE has initiated a testing program to develop and characterize HLW glasses with higher waste loadings for more diverse waste compositions [1, 3]. The initial results of the program have demonstrated the feasibility of higher waste-loading glasses [4]. It is expected that these higher waste loading glasses will reduce the HLW canister production requirement by 25% or more by increasing the waste loading from an average of about 25 wt% to greater than 33 wt% (based on oxide loading) in the glass [4].

While the previous work demonstrated [4] the development of new high waste loading glasses that meet all processing and product quality requirements, in some cases their rate of melting under nominal operating conditions was significantly below the previous WTP HLW melter production goal of 3 MT/d (equivalent to 800 kg/(m²d)) at 1150°C and even farther below the current melter production goal of 3.75 MT/d (1000 kg/(m²d)). The work presented in this report addressed the potential Inconel 690 materials corrosion issues associated with these high waste loading formulations as well as the impact of somewhat higher operating temperatures, since melt rates typically increase with operating temperature. Inconel 690 is the baseline alloy

for the majority of the metallic components in the melter that come into contact with molten glass, including electrodes, bubblers, thermowells, and level detectors.

The four glass compositions investigated in this work are listed in Table 1; they were developed previously [4] for each of the four waste compositions provided by ORP. For each of these compositions, the present work assessed the Inconel 690 corrosion and compatibility aspects of these new formulations at the nominal melter operating temperature of 1150°C and also the potential materials corrosion impacts of operating the HLW melters at slightly higher temperatures (up to 1200°C). Although melt rates generally increase with temperature, so do the challenges imposed on the melter materials of construction and, ultimately, the melter design. The present work is limited to modest temperature increases in order to limit these impacts while still allowing improvements in glass processing rates. Previous tests with a variety of waste feeds in joule heated melters have shown production rate increases of the order of about 1% per °C [5 - 11], depending on feed type and operating conditions. Previous corrosion studies [12 - 28] under a variety of conditions have provided a basis for understanding the corrosion of Inconel 690 and related alloys in borosilicate waste glasses. The general conclusion of these studies has been that Inconel 690 remains the material of choice among the readily available materials for most melter applications; several related alloys, such as MA 758, have been shown to perform better in more demanding applications but are currently much less readily available. The metal corrosion work reported here is designed to expand the knowledge base to include previously untested glass compositions and higher temperatures.

Previously corrosion studies have been performed on Inconel 690 coupons and melter components in Hanford Low Activity Waste (LAW) [13, 16, 26-28] and HLW [14, 25] simulated waste glasses. This base of experience provides guidance as to what one might expect from corrosion studies in the proposed high waste loading HLW waste compositions at elevated temperatures. In particular, the LAW studies at high temperatures [28] indicated increased corrosion at high temperatures but not necessarily at rates that would preclude the use of modestly higher temperatures (e.g., 1200°C). Further, the LAW bubbler lifetime studies performed using the LAW Pilot Melter [26] served to validate the analysis of the behavior of the corrosion of the Inconels observed in the lab-based coupon studies [27]. In particular, the depth of material alteration, including chromium depletion and grain boundary attack, are dominant in determining the lifetime of self-supporting components such as bubblers and thermowells. In the case of electrodes, the actual loss of material is more important than loss of strength. In addition, the results of LAW Pilot Melter tests indicated some variation in Inconel corrosion with waste glass composition.

The WTP HLW studies performed prior to the present work were conducted primarily at the nominal melt temperature (near 1150°C) and with the WTP high-iron baseline compositions. An extensive HLW Pilot Melter study conducted on the baseline compositions [25] examined the behavior of coupons exposed to a variety of melter conditions chosen to represent those to be seen by the major Inconel melter components, and documented corrosion rates within acceptable limits. The study also documented material loss from the bubblers used in the melter campaigns. There were indications of some variability in corrosion rates related to melt composition but the tests could not cleanly separate the effect of individual compositions due to the fact that the test

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scheduling and sequencing was driven by a variety of other test objectives. Despite this, there was some evidence of a compositional dependence, with some compositions showing higher corrosion rates than others, as indicated by a change in weight loss rate with a change in composition.

The HLW glass compositions employed for these earlier WTP materials corrosion studies were developed for the predominantly iron-limited HLW streams that were expected to represent the early feeds to the WTP. Such compositions are much closer to those studied earlier [12 - 28] for applications including the West Valley Demonstration Project (WVDP) and the Defense Waste Processing Facility (DWPF). In contrast, the four compositions that were studied in the present work are markedly different. Assessing the impact of these composition differences and the effects of higher temperature operations are therefore the primary drivers for this work.

1.1 Quality Assurance

The majority of this work was conducted under a quality assurance program based on NQA-1 (1989) and NQA-2a (1990) Part 2.7 that was in place at the VSL. However, during this work, ORP provided direction to move to a quality assurance program compliant with 10 CFR 830 Subpart A, NQA-1 (2000), DOE Order 414.1C, and DOE/RW-0333P, Rev. 18; these changes were implemented prior to the completion of this work. In both cases, the program was supplemented by corresponding Quality Assurance Project Plans (QAPP) for ORP work that is conducted at VSL, which also define the test and procedure requirements by which the testing activities are planned and controlled. The VSL QA program is supported by VSL standard operating procedures that were used for this work. Since this work is not HLW waste form qualification affecting, the requirements of DOE/RW-0333P are not applicable to this work.

SECTION 2 EXPERIMENTAL METHODS

2.1 Experimental Design and General Approach

As outlined in the Test Plan [2], the objectives of this work were to investigate the corrosion resistance of Inconel 690 in the new, non-Fe-limited waste glasses at and above the typical HLW melter operating temperatures and to assess the viability of operating the HLW melters at slightly higher temperatures, which would have the benefit of increased processing rate and waste loadings. Specifically, the glass-contact corrosion of Inconel 690 was tested at temperatures of 1150°C, 1200°C, and 1230°C for 7 days, and at 1200°C for 14 days in four representative glass compositions (Table 1). The test coupons were then sectioned and analyzed for their dimensional loss and internal structural damage to determine the effects of test temperature, time, and glass composition. In addition, the metal corrosion under an imposed electrical field at the upper end of the typical current density design range was examined at 1200°C for 3 days to assess the additional effects due to electrical corrosion.

Generally, Inconel 690 reacts with molten glass rather slowly at typical melter operating temperatures, which is as intended. However, this presents challenges in assessing the corrosion damage to the alloy by a molten glass, particularly if it is judged solely from the dimensional loss determined in a short term laboratory test. The interior structural damage incurred in the corrosion process, which can be assessed by electron microscopy, provides valuable additional information and is often more indicative of the corrosion process. The key parameters for assessing the corrosion damage to a Ni-Cr based super alloy such as Inconel 690 are:

- The dimensional loss of the test coupons;
- Internal structural degradation, as reflected by grain boundary damage, oxidation, or glass melt intrusion;
- Internal compositional alteration, as reflected by dealloying or sensitization and, in particular, in the depletion of chromium, which is a critical element in Inconel 690; and
- Oxide scale formation and characteristics.

In previous work, the depth of Cr-depletion inside the reacted Inconel 690 coupon was identified as the most indicative parameter for assessing the long term corrosion rate for representative LAW formulations [28].

Table 2 summarizes the corrosion tests performed in this work and the corresponding test conditions.

2.2 Sample Preparation

2.2.1 Coupon Preparation for Standard Metal Corrosion Tests

Rectangular coupons of Inconel 690 were machined from the bulk material and their surfaces polished (Figure 1). The dimensions of the coupons are 0.300 by 0.150 inch in cross-section and of sufficient length to be immersed in the molten phases to a depth of 0.9 inch (Figure 2). All dimensions of the coupons were measured by micrometer to better than 0.5 mil before the tests. The precision of the parallel surface was better than 0.001 inch.

2.2.2 Coupon Preparation for Electrical Metal Corrosion Tests

These tests employ a concentric-cylinder geometry. The test coupon, which forms the center electrode for these tests, was machined from bulk Inconel 690 into a round pin with a diameter of 0.195 mm and a length of 22 mm. Inconel wire was welded to one end of the pin for electrical connection. The pin with attached wire was then inserted into an alumina protective sleeve and made to protrude from the sleeve by 10 mm (Figure 3).

2.2.3 Glass for Corrosion Tests

During the development of the four compositions that were selected for the present work [4], an inventory of each of the glasses was produced during DuraMelter 100 campaigns. Sufficient quantities of homogeneous, previously analyzed, glasses were used to perform the present testing.

2.3 Metal Glass-Contact Corrosion Tests

2.3.1 Standard Metal Glass-Contact Corrosion Test

Corrosion tests with molten glass were conducted using the Catholic University of America (CUA)/Vitreous State laboratory (VSL) technical procedure TPI-GMC [29] using the experimental arrangement shown schematically in Figure 2. The experimental setup consists of a 50 ml platinum crucible placed into a quartz holder. On the top of the crucible there is a cover with a 5 mm slot. The coupon is placed through the slot and suspended by a rod that is placed through a hole drilled through one end of the coupon. For each corrosion test, 70 grams of glass is melted at 1150°C (nominal) for 30 minutes; this quantity gives an S/V ratio for these tests of 0.15 cm⁻¹ and the crucible is filled to ¾ of its height (29 mm) with glass. The coupon with the lid is preheated to 800°C, allowing an oxide layer to form on the coupon, which is then placed into the crucible with the molten glass. The experimental setup is then placed into a furnace that is preheated to the desired test temperature (1150°C, 1200°C, or 1230°C). After the designated period of time, the setup is removed from the furnace, the coupon is extracted from the glass, and the glass melt is poured into a graphite mold for further analyses. The coupon with the glass

coating is then embedded in epoxy. For the extended tests, the coupon and lid are removed from the initial crucible after 7 days, excess glass is allowed to drip off the coupon, and the coupon with lid are placed in a crucible containing fresh glass. The glass from the first crucible is poured into a graphite mold and sampled for further analysis. After the second 7-day period, the coupon and glass are removed according to the same procedure for further analysis.

2.3.2 Electrical Metal Glass-Contact Corrosion Test

Corrosion tests in the presence of an electric field were conducted in molten glass at 1200°C. The tests followed CUA/VSL technical procedure TPI-EMC [30], which employs a concentric-cylinder geometry. The outer cylinder is fabricated from Inconel 690 and forms both the container for the molten glass and one of the electrodes. The inner cylinder, which is of much smaller diameter, is fabricated from the test material and forms the second electrode. In this way, a high current density is achieved at the test coupon while maintaining a low current density at the container and a relatively low total current, which avoids excessive joule heating. The entire assembly is installed in a vertical tube furnace set at the desired test temperature. The center electrode with attached wire is introduced inside the tube furnace after being inserted into an alumina protective sleeve and made to protrude from the sleeve by 10 mm. Another Inconel wire is welded to the top edge of the Inconel 690 crucible for electrical connection. During the test, the center electrode is positioned at the center of the crucible and introduced into the glass melt to the depth of 12 mm, which allowed the alumina sleeve surrounding the center electrode to extend 2 mm into the melt. This 2-mm immersion helps to prevent enhanced corrosion of the center electrode at the air-glass melt line during the tests (Figure 3).

The electric circuit for the tests is shown in Figure 4. A 60 Hz AC source was used to maintain a current density of 6 A/inch² at the center electrode pin. Over the entire duration of the electrical corrosion experiments (three days at 1200°C in ambient condition), the actual current passing through the corrosion cell is controlled by monitoring the voltage across a precision resistor that was in series with the corrosion cell. The actual current passing through the circuit to achieve the targeted 6 A/inch² current density was 0.6 A.

After the test coupon was removed from the corrosion setup, it was sectioned at 1 mm, 5 mm, and 9 mm from the bottom tip and the cross-sections were prepared for subsequent microscopic analysis.

2.4 Optical Microscopy

After each corrosion test, the reacted coupons were embedded in resin and then sectioned at the mid-point (Figure 1) and polished. Both halves of the sectioned coupons were examined using a microscope for corrosion characteristics (e.g., morphology of new, modified, and original phases, the texture of the reacted alloys, etc.). The thickness of the reacted coupon was measured using a measuring microscope, which has a precision of better than 0.05 mil (1.27 µm). Typically, 10 transverse lines were measured perpendicular to the length of the coupon. The

overall uncertainty associated with these measurements is about 0.5 mil. The dimensional loss is calculated as half of the difference of the measured widths between the original and reacted coupons near the glass line (or sometimes referred as the *neck* if such a feature develops) and at the location corresponding to half of the immersed length of the coupon (referred to as the *half-down* position). The sectioned coupons were further characterized using Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy (SEM-EDS).

2.5 SEM/EDS

Scanning electron microscopy (SEM; JEOL JMS 5910LV) with a digital imaging system was used to characterize the microstructure of alloy materials after corrosion. Typical magnifications used ranged from 25× to 5,000×. Energy dispersive x-ray spectroscopy (EDS) was used to analyze the chemical composition of the glass, crystalline oxide phases, and the corroded materials. SEM measurements typically provide better results on the structurally damaged zone than does optical microscopy. The elemental profiles were obtained by either EDS line-scanning or point analysis, from the glass-metal interface to the center of the coupon.

2.6 Compositional Analysis

The glass samples were analyzed before and after the corrosion experiments. This information provides an indicator of the corrosion progress that is complementary to the coupon analyses.

The primary method used for glass analysis was X-ray fluorescence (XRF) on powdered glass samples. A Thermo Scientific ARL 9400 wavelength dispersive XRF spectrometer with extended light-element capability was used for this purpose. Since lithium and boron are not determined by this method, these measurements were supplemented as necessary by digestion and solution analysis. In this method, the glass samples are subjected to microwave-assisted total acid dissolution in Teflon vessels. Twenty milliliters of a 1:5 mixture of concentrated HF:HNO₃ is diluted to 50 ml and used for the dissolution. The resulting solutions were analyzed by direct current plasma-atomic emission spectroscopy (DCP-AES); anions are determined by ion chromatography (IC).

2.7 X-Ray Diffraction Analysis

Powder samples of the glasses after corrosion tests were examined by X-ray diffraction (XRD) for possible crystallization. About one gram of glass sample was used for XRD analysis. The sample was ground, using a ceramic or agate pestle and mortar, to pass through a 200-mesh sieve. The glass sample was mounted on a goniometer. The settings for the XRD were a 2θ angle from 5° to 80° at 0.02° steps and 2 seconds count time at each step. After the powder pattern was collected, JADE (version 5) was used for identification of possible crystalline phases.

SECTION 3 RESULTS AND DISCUSSION

3.1 Standard Glass Contact Metal Corrosion

Standard glass contact metal corrosion tests were performed for all four glasses at 1150, 1200 and 1230°C for seven days, and at 1200°C for an extended 14 day period (Table 2). The test results for each glass are reported in turn below. Comparison of the corrosion test results for the four glasses are given in Section 3.3.

3.1.1 Inconel 690 Corrosion in Bi-Limited HLW Glass Melts

The Bi-limited waste glass (BLL-G-46B) has the highest levels of Bi and Ni among the four waste glasses (Table 1). The Inconel 690 coupons after 7 day corrosion tests displayed little dimension loss at 1150°C and 1230°C (around 1 mil, as shown in Table 3) but showed moderate loss at the half-down and near glass surface region at 1200°C after 7 days and 14 days. In both cases, more than one mil (up to 4 mil for the 14-day test) of dimension loss was observed. It should be noted that the term *near glass surface* loss instead of the traditional *neck* loss was preferred herein due to the fact that the typical neck did not develop in the reacted metal coupons in this study.

Scales of chromium oxide and spinel phases developed on the surface of Inconel 690 in the Bi-limited glass melt in all standard corrosion tests (Tables 3 and 5, Figures 5 and 8). Similar to the previous observations [22, 28], a continuous oxide layer composed predominantly of Cr₂O₃ grew from the metal surface and was coated with a thinner spinel layer that was adjacent to the glass melt. Both the chromium oxide and spinel layers grow thicker with increasing temperature and test duration (from 7 to 14 days).

The internal oxidation and structural damage of Inconel 690 are typically reflected in the grain boundary damage and selective depletion of chromium from the interior of the alloy. Grain boundary damage, as revealed by SEM (Figures 6 and 8), is generally evident with numerous pitted pockets near the surface and the development of occlusions of oxide phases more than 100 microns from the remaining surface of the coupon. There is no clear trend that indicates an increased depth of grain boundary damage with temperature or test duration. It is, however, notable that the oxide formation (indicated by the darker occlusions near the metal surface) becomes more abundant after 14 days at 1200°C. The depletion of chromium from Inconel 690 is easily identifiable from the SEM/EDS line scans that were collected near the half-down location perpendicular to the coupon surface. As shown in Figures 7 and 8 and summarized in Table 3, the Inconel 690 coupons lost more than 1/3 of the chromium near the surface, with the depleted region extending up to 500 micron deep at 1150 and 1200°C. Both the extent of the depletion at the surface and the depth of the depletion are greater after 7 days at 1230°C and after 14 days at

1200°C. The line scan data of Cr depletion were confirmed by more precise (but more time consuming) SEM/EDS point analysis in the regions near the surface; these results are in good agreement (Figures 7 and 8).

The results from the glass composition analysis did not show clear trends of the extent of the metal dissolution with either temperature or test duration (Table 4). It is noted, however, that the Cr₂O₃ analysis by XRF for glass samples after corrosion differed considerably from those by DCP. While the XRF values are generally in agreement with the targeted values, the DCP values tend to be about half of the target. This discrepancy decreases with increasing test temperature. This discrepancy is believed to result from the different methods used for sample preparation. In particular, the acid digestion for DCP is designed for glass sample analysis, which is not very effective in dissolution of certain types of non-silicate oxide crystals such as spinels. In contrast, a powdered solid is used for XRF. XRD powder patterns of the glass samples used for XRF showed a clear diffraction peak of Cr-rich spinel at a 2θ angle of 36° and, furthermore, that the relative intensity of the spinel peak decreases with increasing temperature, a trend parallel to that defined by glass Cr₂O₃ wt% by DCP analysis. It is concluded, therefore, that the XRF analysis of the glass samples after metal corrosion experiments reflects the chemical makeup of the bulk materials that include both the glass and Cr-rich spinel, whereas the DCP analysis is more indicative of the composition of the glass phase. As shown in Table 4, there is no clear trend in glass composition by DCP analysis for corrosion tests at different temperatures and durations.

3.1.2 Inconel 690 Corrosion in Cr-Limited HLW Glass Melts

The Cr-limited waste glass (BLL-G-113A) has the highest level of Cr among the four waste glasses (Table 1). The Inconel 690 coupons after 7 and 14 day corrosion tests displayed little dimension loss, around 1 mil at 1150°C and 1230°C (Table 3). There is no clear indication of increased dimension loss with either increasing temperature or test duration.

Essentially continuous scales of primarily chromium oxide developed on the surface of Inconel 690 coupons in this glass. In contrast to the scale observed in the tests with the Bi-limited glass, the spinel layer was absent in all standard corrosion tests with the Cr-limited glass (Tables 3 and 6, Figures 9 and 12). In the glass adjacent to the chromium oxide layer, acicular crystals observed in the 1200°C 7-day test were identified as Cr₂O₃ with minor amounts of Fe₂O₃. The oxide layer grows thicker with increasing temperature and test duration (from 7 to 14 days).

Grain boundary damage is evident by SEM (Figures 10 and 12) with pitted pockets near the surface and the development of occlusions of oxide phases more than 100 micron from the remaining surface of the coupon. It appears that internal oxidation increases significantly when temperature is above 1200°C (at 1230°C in Figure 10-c), as shown by deeper and more densely populated oxide occlusions, and when test time is longer (14 days vs. 7 days), as indicated by more pronounced surface pitting (Figure 12). The depletion of chromium from Inconel 690 is clearly evident from the SEM/EDS line scans that were collected near the half-down location perpendicular to the coupon surface. As shown in Figures 11 and 12 and summarized in Table 3,

at 1150 and 1200°C, Inconel 690 lost more than 1/4 of the chromium from the surface of the coupon, with the depleted region extending up to 450 microns deep. The extent of the depletion near the surface and the depth becomes more extensive at 14 days at 1200°C (Figure 12), with 40% Cr loss near the surface and extending up to 600 microns deep. It is not clear why the surface depletion in the 1230°C test was less than that observed in the 1200°C test. However, the line scan data indicate a considerably deeper Cr depletion (up to 600 microns) that is comparable to that observed in the 14 day test at 1200°C.

A similar discrepancy between the DCP and XRF glass analysis for Cr₂O₃, albeit to a less degree, to that observed with the Bi-limited glass was seen with the Cr-limited glass. However, in this case, the XRD powder patterns of the glass samples used for XRF did not show the characteristic diffraction peak of Cr-rich spinel. This is consistent with the fact that the spinel layer was absent in the metal scale and, instead of spinel, escholaite (Cr₂O₃) was observed within the glass near the metal scale. Therefore, minor crystallization of a Cr₂O₃-rich phase could have contributed to the observed disparity between the XRF and DCP analyses. Therefore, as before, the DCP data probably better reflect the amount of Cr dissolved in the glass. As shown in Table 4, there is no clear trend in glass composition by DCP for corrosion tests at different temperatures and durations.

3.1.3 Inconel 690 Corrosion in Al/Na-Limited HLW Glass Melts

The Al/Na-limited waste glass (BLN-G-129A) is the second highest in Al₂O₃ and Cr₂O₃ among the four waste glasses (Table 1). The Inconel 690 coupons after 7 and 14 day corrosion tests displayed little dimension loss, around 1 to 2 mil at 1150°C and 1230°C (Table 3). There is no clear indication of increased dimension loss with either increasing temperature or test duration.

Essentially continuous scales of primarily chromium oxide developed on the surface of Inconel 690 coupons in this glass. In contrast to the scale observed in the tests with the Bi-limited glass, the spinel layer was absent in all standard corrosion tests with the Al/Na-limited glass. (Tables 3 and 7, Figures 13 and 16). In the glass adjacent to the chromium oxide layer, acicular crystals observed at 1230°C in the 7-day test and at 1200°C in the 14-day test were identified as Cr₂O₃ with minor amounts of Fe₂O₃. The oxide layer grows thicker with increasing temperature and test duration (from 7 to 14 days).

Grain boundary damage is evident by SEM (Figures 14 and 16), with pitted pockets near the surface and the development of occlusions of oxide phases more than 100 microns from the remaining surface of the coupon. It appears that internal oxidation increases significantly when temperature is above 1200°C (at 1230°C in Figure 14-c), as shown by deeper and more densely populated oxide occlusions, and when the test duration is extended (14 days vs. 7 days), as indicated by the more pronounced surface pitting (Figures 14 and 16). The depletion of chromium from Inconel 690 is evident from the SEM/EDS line scans that were collected near the half-down location perpendicular to the coupon surface. As shown in Figures 15 and 16 and summarized in Table 3, at all three test temperatures (1150, 1200, and 1230°C), Inconel 690 lost

more than 1/3 of the chromium from the surface with the depleted region extending up to 500 microns deep. The depletion region extended deeper into the alloy after 14 days at 1200°C (up to 550 microns, as shown in Figure 16).

A similar discrepancy between the DCP and XRF glass analysis for Cr₂O₃, albeit to a less degree, to that observed with the Bi-limited glass was seen with the Al/Na-limited glass. However, in this case, the XRD powder patterns of the glass samples used for XRF showed only a very weak diffraction peak of Cr-rich spinel for the 1150°C test sample and no obvious peaks for the 1200 and 1230°C test samples. This is consistent with the fact that the spinel layer was absent in the metal scale and, instead of spinel, escholaite (Cr₂O₃) was observed within the glass near the metal scale. Therefore, minor crystallization of a Cr₂O₃-rich phase could have contributed to the observed disparity between the XRF and DCP analyses. Therefore, as before, the DCP data probably better reflect the amount of Cr dissolved in the glass. As shown in Table 4, there is no clear trend in glass composition by DCP for corrosion tests at different temperatures and durations.

3.1.4 Inconel 690 Corrosion in Al-Limited HLW Glass Melts

The Al-limited waste glass (BLM-G-145A) contains the most Al₂O₃ among the four waste glasses (Table 1). The Inconel 690 coupons after 7 day corrosion tests displayed little dimension loss at 1150°C, 1200, and 1230°C (Table 3). There is no clear indication that the dimension loss increases with either increasing temperature or test time.

Scales consisting of chromium oxide and spinel phases developed on the surface of Inconel 690 coupons in the Al-limited glass melt in all standard corrosion experiments (Tables 3 and 8, Figures 17 and 20). A continuous oxide layer, which is predominantly Cr₂O₃, grew from the metal surface with a thinner spinel top coat adjacent to glass melt. Both the oxide and spinel layers grow thicker with increasing temperature and test duration (from 7 to 14 days).

Grain boundary damage is evident by SEM (Figures 18 and 20), with pitted pockets near the surface and the development of occlusions of oxide phases more than 100 micron from the remaining surface of the coupon. It appears that internal oxidation increases significantly when the temperature is above 1200°C (at 1230°C in Figure 18-c), as shown by deeper and more densely populated oxide occlusions, and when the test time is longer (14 days vs. 7 days), as indicated by more pronounced surface pitting (Figures 18 and 20). The depletion of chromium from Inconel 690 is evident from the SEM/EDS line scans that were collected near the half-down location perpendicular to the coupon surface. As shown in Figures 19 and 20 and summarized in Table 3, at 1150 and 1200°C, Inconel 690 lost more than 1/3 of the chromium from the surface with the depleted region extending up to 450 microns deep. The depletion extended about 200 microns deeper into the alloy when test temperature was increased to 1230°C (7 days) or when the test duration was extended to 14 days (vs. 7 days at 1200°C; Figures 19, and 20). Moreover, in both cases, the magnitude of the Cr depletion near the surface decreases (Figure 19-c and 20).

Similar to the discrepancy observed in the Bi-limited glass experiments, the Cr_2O_3 analysis by XRF and DCP for glass samples after the corrosion tests differed considerably. The XRD powder patterns of the glass samples used for XRF show a clear diffraction peak of Cr-rich spinel at a 2θ angle of 36° and, furthermore, the relative intensity of the spinel peak decreases with increasing temperature, a trend parallel to that defined by the glass Cr_2O_3 wt% by DCP analysis. Therefore, as before, the DCP data probably better reflect the amount of Cr dissolved in the glass. As shown in Table 4, there is no clear trend in glass composition by DCP analysis for corrosion tests at different temperatures and durations.

3.2 Electrical Glass Contact Metal Corrosion

Glass contact metal corrosion in the presence of an electric field was tested for three of the four glasses at 1200°C for three days (Table 2). The test results for the three selected glass systems are discussed together in this section.

The Inconel 690 coupons after 3-day corrosion tests displayed little dimension loss at 1200°C (about 1 to 2 mil, as listed in Table 9) and there was no dependence of the dimension loss on glass composition.

The scales on Inconel 690 coupon for the Bi-limited glass test were not preserved successfully during sectioning and polishing of the corroded metal pin. As a result, for this glass, only the cross sections of Inconel 690 alloy were imaged (Figure 21). Continuous chromium oxide scales were evident on the surface of Inconel 690 in the Cr-limited and Al/Na-limited glass melts at all three sectioned locations (near surface, near tip, and half-down; Tables 9-13, Figures 22 and 23). Other than occasional spinel crystals scattered in the nearby glass for the Cr-limited glass, no spinel layer was present in the scale for the Al/Na-limited glass tests and only a very thin film of spinel was present on top of the chromium oxide layer for the Cr-limited glass tests. For both glass systems, the thickness of the chromium oxide scale is close to that measured from the standard 7-day corrosion tests for the corresponding glasses (Table 9 and Table 3).

Grain boundary damage is evident in the Inconel 690 coupons from the three tests (SEM images in Figures 24, 25, and 26), with pitted pockets near the surface and the development of occlusions of oxide phases in a zone around 50 to 100 micron from the remaining surface of the coupon, which is considerably shallower than that measured from the 7 day standard corrosion tests at the same test temperature (typically more than 100 microns). The extent of internal oxidation does not appear to have been significantly affected by the addition of the electrical current. The depletion of chromium from Inconel 690 is evident from the SEM/EDS line scans that were collected near the half-down location perpendicular to the coupon surface. As shown in Figure 27 and summarized in Table 9, Inconel 690 in the Bi-limited glass melt lost about 1/3 of chromium from the surface with a depleted region extending up to 250 microns deep. The surface Cr depletion is worse for the Al/Na-limited glass (more than 40% loss and 290 microns deep), and the worst for the Cr-limited glass (~50% surface depletion and 290 microns deep). Overall, the Cr-depletion depths for the three glass tests are considerably shallower than those measured from the standard 7 day tests at the same temperature (Table 9 and Table 3). However,

the coupons after the 3-day electrical corrosion tests have lost more chromium from the surface as compared to their counterparts in the standard 7-day tests.

The glass samples after the electrical corrosion tests all show considerable contamination resulting from contact with the Inconel 690 outer electrode (as the crucible, which has a much larger surface area than the coupons). As shown in Table 10, compared to the target values, nickel, which is one of the key Inconel components, increased by a few wt%, whereas Cr decreased. Moreover, similar to the discrepancy observed in the standard metal corrosion tests, the Cr₂O₃ analysis by XRF and DCP for glass samples after the corrosion tests differed considerably, with the values by XRF consistently higher than those by DCP. The XRD powder patterns of the glass samples used for XRF showed that a diffraction peak of Cr-rich spinel at a 2 θ angle of 36° is evident for the Bi-limited and Cr-limited glass samples and is marginally visible for the Al/Na-limited glass sample. The large amounts of Ni would likely also have contributed to spinel formation. Because of the large surface area of the crucible, it is not possible to separate the contributions from the outer electrode and the center electrode to the observed changes in glass composition.

3.3 Evaluation of Implications for Longer-Term Corrosion

As discussed above, while the dimension loss is the most straightforward measure of the potential service life of an alloy, this parameter presents a number of issues and limitations for small-scale coupon tests with limited durations. Even in actual service, the dimension loss can be minimal but the internal damage to the alloy can result in such extensive degradation of its native properties as to render it unfit for service (e.g., due to grain growth and embrittlement and/or chromium loss and loss of passivation). Accordingly, it is important to supplement the simple dimension loss measurements with other information, as was done in the present work.

As shown in Tables 3 and 9, the measured coupon dimension losses near the glass surface and at the half-down locations are essentially all clustered around 1 mil, with no clear dependence on either test duration or temperature; the one exception is for the Bi-limited glass, in which the dimension loss was measured at as much as 4 mil at 1200°C for the 14-day test. The highest value corresponds to about one-tenth of an inch per year, which is well within the acceptable range for electrodes. However, as noted above, this addresses only one aspect of the corrosion process.

Internal damage to the alloy includes effects due to grain boundary damage and the associated internal oxidation; de-alloying/sensitization of Ni-Cr alloys and, in particular, the selective depletion of Cr; and scale characteristics (such as phase assembly and thickness, scale integrity, etc.). It turns out that some of the parameters are correlated. As shown in Figure 28, the Cr-depletion depth inside the Inconel 690 metal is found to be roughly proportional to the thickness of the oxide scale that develops on the metal surface. Such a correlation is reasonable considering that the chromium oxide that constitutes the majority of the scale originates from the Inconel 690 itself and forms at the expense of a growing Cr-depletion zone in the alloy. As proposed in previous studies of Inconel 690 corrosion [22, 28], the Cr-depletion depth provides a

useful indicator of the glass corrosion damage for the Inconel 690 beyond simple dimension loss. The chromium content of the super alloys such as Inconel 690 is a critical contributor to its corrosion resistance and in protecting the alloy from the strongly oxidizing molten glass solvent [23]. Metal corrosion increases as the chromium content falls and accelerates drastically once the chromium content in the Inconel alloy falls below about 20 wt% [23].

Figure 29, shows the Cr-depletion depths after the standard 7 day corrosion tests plotted versus the test temperatures. Interestingly, the depth measured from all four glasses displayed very little change as temperature was increased from 1150°C to 1200°C, but increased by 25 to 40% as temperature was further increased from 1200°C to 1230°C. These results suggest that the corrosion resistance of Inconel 690 does not deteriorate significantly between the normal melter operating temperatures of 1150°C and 1200°C, but is impacted at higher temperatures. The four glasses tested can be ranked by Cr-depletion depth as follows:

- Bi-limited glass is the most corrosive, with a depth of 500 microns for 7-day test at both 1150 and 1200°C;
- Al-limited glass, with a depth of 450 microns at both 1150 and 1200°C;
- Cr-limited glass with depth of 400 to 450 microns, at 1150 and 1200°C, respectively;
- Al/Na-limited glass with a depth of 350 microns at both 1150 and 1200°C.

It is probably not a coincidence that the two least corrosive glasses have the higher Cr contents among the four glasses; it is interesting to note that the spinel layer is missing from the scales on the metal coupons for these same two glasses.

The Cr-depletion data are both sufficiently quantitative and extensive as to provide an additional assessment of the potential service life of Inconel 690 at the proposed elevated operating temperature of 1200°C. As discussed earlier, the results for Inconel 690 coupons tested in the presence of 6 A/inch² current density did not exhibit significantly different corrosion damage from those tested at the same temperature, but without the electrical field. Therefore, if we assume that the test duration is the more dominant difference, we can analyze the 3-day electrical corrosion test data together with the data from the 7-day and 14-day standard corrosion tests in order to assess the time dependence. The results show clearly that the Cr-depletion depth for all four glasses at 1200°C increases parabolically with time with the depth proportional to the square root of time, which is typical of a diffusion-limited process. This behavior is shown in Figure 30. In view of the nearly linear correlation observed between the Cr depletion depth and metal scale thickness (Figure 28), it is evident that the growth of the oxide scale on the metal surface will also follow the square root dependence on time¹. Thus, the observed parabolic time dependence suggests a diffusion limited process for the growth of the metal scale and the internal Cr depletion. Given that the growth of the Cr₂O₃ scale is fueled by depletion of Cr from inside of the Inconel coupon, it is reasonable to imagine a process of transporting Cr from the interior of Inconel 690 to the surface to form Cr₂O₃ oxide scale. Furthermore, if, assuming that the oxidation of Cr on the metal surface is fast in comparison to Cr diffusion through the Ni-based

¹ This highlights another issue with a simple dimension loss measurement: whether or not the thickness of the oxide layer is included.

Inconel 690, then the depletion of Cr, which is critical for internal metal damage, should be controlled by the diffusion coefficient of Cr in the Ni matrix. The diffusivity of Cr through Ni media has been measured and the value from the published data is $2.5 \times 10^{-10} \text{ cm}^2/\text{s}$ at 1200°C [31]. The Cr diffusion coefficient can be estimated from the Cr depletion depths measured in the present work, which gives a value of about $3.0 \times 10^{-9} \text{ cm}^2/\text{s}$. The one order of magnitude difference is likely due to the contribution of grain boundary diffusion (notice the inter-granular damage, as revealed in the SEM images), which is much faster than bulk diffusion.

From the experimental data, and assuming that diffusion continues to play the dominant role in leaching Cr from Inconel 690, the Cr depletion depth at any time can be estimated to assess the potential long-term damage. In Figure 30, the parabolic dependence of the Cr-depletion depth on time for the four glass tests are plotted together. From the figure, it can be seen that Inconel 690 is predicted to suffer up to about 4-5 mm of Cr depletion in a 2-year service period and about 1 cm (7-8 mm) of Cr depletion for 5 years service at 1200°C . It should be noted, however, that this estimate is based on the assumption of a continuous growth of surface scale and internal diffusion. It does not include effects such as spalling off of the weakly adhered scale to expose the fresh metal surface, or grain boundary damage that may facilitate more rapid mass transport, or eventual dimension loss after extensive Cr loss. Nevertheless, a loss of 1 cm over 5 years is in general agreement with the loss observed from electrodes that were in continuous service in the LAW Pilot Melter ($1.27 \text{ cm}/5 \text{ years}$), which experienced more corrosive LAW glass compositions, albeit at 1150°C .

3.4 Effect of Phosphorus on Inconel 690 Corrosion

As noted above, the Bi-Limited glass was found to be the most corrosive of the four compositions tested, both in terms of dimension loss and Cr-depletion. The Bi-limited glass contains the highest amount of phosphorus of the four glasses and phosphidation is a well known degradation mechanism in high-Cr alloys including Inconels [23]. Phosphate glasses, which employ phosphorus instead of silicon as the primary glass former, have been considered for HLW vitrification for many years. Phosphate glasses were originally selected for the German-Belgian PAMELA process but were abandoned in favor of borosilicate glass; however, phosphate glasses have been employed in the former Soviet Union in melters that employ molybdenum electrodes [32]. Phosphate glasses for waste vitrification saw a brief resurgence in the 1980s with the lead-iron-phosphate glasses [32] and more recently with iron phosphate glasses [33, 34]. However, materials compatibility issues are an important factor for processing phosphate glasses and it is not clear that Inconels, which were selected as appropriate for borosilicate glasses, would be satisfactory materials for phosphate melts.

Day and his coworkers have conducted corrosion tests of Inconel 690 in several of their iron phosphate glasses [33, 34] designed for high-sodium Hanford LAW. According to their assessment, Inconel 690 corrosion damage in their iron phosphate glasses is comparable to that observed for typical borosilicate glasses in the fully submerged condition. However, their assessment was based primarily on weight loss, which is probably even less indicative of the extent of the corrosion damage than is dimension loss because of the potential for offsetting

weight *gain* (e.g., by oxidation) as the corrosion proceeds. In addition, the metal corrosion rate was determined at 1050 or 1025°C and compared to that of borosilicate glass at 1150°C. Kim et al. have investigated iron phosphate glass as an alternative waste form for Hanford LAW [34]. Their metal corrosion data indicate a similar corrosion rate for Inconel 690 in the fully submerged condition. However, in the same report, Kim et al. note that Inconel 690 was corroded rapidly in iron phosphate glass formulated for LAW at 1025°C if part of the alloy was exposed above the glass line. This result compares very unfavorably to the very small dimension losses determined in the present work for Inconel 690 at temperatures of 1150°C to 1230°C in all four HLW glass melts at both the half-down and near glass surface locations.

Previous Inconel 690 corrosion tests performed at VSL with iron phosphate glasses developed by Day et al. showed very extensive damage [35; included as Appendix A]. That work showed dimension losses some 30 times greater than for typical borosilicate glasses and even after 3 days there was massive grain growth, scale as thick as 1200 microns, and remarkably extensive damage in the vapor space above the melt. Inconel damage is therefore a serious concern with high-phosphate glasses.

SECTION 4 SUMMARY AND CONCLUSIONS

Metal corrosion tests were conducted with four high waste loading non-Fe-limited HLW glass compositions. The results at 1150°C (the WTP nominal melter operating temperature) show corrosion performance for all four glasses that is comparable to that of other typical borosilicate waste glasses, including HLW glass compositions that have been developed for iron-limited WTP streams. Of the four glasses tested, the Bi-limited composition shows the greatest extent of corrosion, which may be related to its higher phosphorus content. Tests at higher temperatures suggest that a moderate elevation of the melter operating temperature (up to 1200°C) should not result in any significant increase in Inconel corrosion. However, corrosion rates did increase significantly at yet higher temperatures (1230°C). Very little difference was observed with and without the presence of an electric current density of 6 A/inch², which is the typical upper design limit for Inconel electrodes. The data show a roughly linear relationship between the thickness of the oxide scale on the coupon and the Cr-depletion depth, which is consistent with the chromium depletion providing the material source for scale growth. Analysis of the time dependence of the Cr depletion profiles measured at 1200°C suggests that diffusion of Cr in the Ni-based Inconel alloy controls the depletion depth of Cr inside the alloy. The diffusion coefficient derived from the experimental data agrees within one order of magnitude with the published diffusion coefficient data for Cr in Ni matrices; the difference is likely due to the contribution from faster grain boundary diffusion in the tested Inconel alloy. A simple diffusion model based on these data predicts that Inconel 690 alloy will suffer Cr depletion damage to a depth of about 1 cm over a five year service life at 1200°C in these glasses.

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Table 1. Starting Glass Compositions (XRF analysis from [4]).

Waste type	Bi limited	Cr limited	Al-Na limited	Al limited
Sample ID	BLL-G-46B	BLL-G-113A	BLN-G-129A	BLM-G-145A
Ag ₂ O	<0.01	-	-	-
Al ₂ O ₃	11.48	9.07	20.74	22.29
B ₂ O ₃	11.29	15.88	18.29	15.20
BaO	0.03	0.02	0.07	0.32
Bi ₂ O ₃	6.67	2.90	1.17	1.30
CaO	0.87	0.83	1.10	5.87
CeO ₂	<0.01	-	-	-
Cl	0.05	-	-	-
CdO	-	-	<0.01	0.01
Cr ₂ O ₃	0.51	1.19	0.78	0.52
F	0.49	0.49	0.18	0.41
Fe ₂ O ₃	7.38	5.06	3.12	6.16
K ₂ O	0.54	5.53	0.70	0.42
Li ₂ O	0.18	3.47	3.58	3.57
MgO	0.50	0.22	0.26	0.43
MnO	0.15	0.03	0.05	0.03
Na ₂ O	15.23	7.68	12.82	9.80
Nd ₂ O ₃	0.05	<0.01	0.01	0.01
NiO	1.67	0.53	0.16	0.33
P ₂ O ₅	5.06	1.48	1.99	1.09
PbO	0.30	0.17	0.10	0.37
SiO ₂	36.27	44.82	34.17	31.09
SnO ₂	0.01	-	-	-
SO ₃	0.43	0.41	0.16	0.15
SrO	0.03	<0.01	-	-
TiO ₂	0.19	0.03	0.16	0.05
ZnO	0.20	0.11	0.17	0.09
ZrO ₂	0.42	0.07	0.20	0.49
Total	100	100	100	100

"-" empty data field

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Table 2. Summary of Inconel 690 Corrosion Experiments.

Waste type	Start Glass ID	Glass ID after 7-day Corrosion	Glass ID after 14-day Corrosion	Inconel 690 ID after Corrosion	Test Conditions
Bi-limited	BLL-G-46B	HW-Bi-1150	-	INC-Bi-1150	7 days at 1150°C
Cr-limited	BLL-G-113A	HW-Cr-1150	-	INC-Cr-1150	
Al-Na-limited	BLN-G-129A	HW-AN-1150	-	INC-AN-1150	
Al-limited	BLM-G-145A	HW-Al-1150	-	INC-Al-1150	
Bi-limited	BLL-G-46B	HW-Bi-1200	-	INC-Bi-1200	7 days at 1200°C
Cr-limited	BLL-G-113A	HW-Cr-1200	-	INC-Cr-1200	
Al-Na-limited	BLN-G-129A	HW-AN-1200	-	INC-AN-1200	
Al-limited	BLM-G-145A	HW-Al-1200	-	INC-Al-1200	
Bi-limited	BLL-G-46B	HW-Bi-1230	-	INC-Bi-1230	7 days at 1230°C
Cr-limited	BLL-G-113A	HW-Cr-1230	-	INC-Cr-1230	
Al-Na-limited	BLN-G-129A	HW-AN-1230	-	INC-AN-1230	
Al-limited	BLM-G-145A	HW-Al-1230	-	INC-Al-1230	
Bi-limited	BLL-G-46B	HW-Bi-7-1200	HW-Bi-14-1200	INC-Bi-14-1200	14 days at 1200°C, with glass replenished after 7 days
Cr-limited	BLL-G-113A	HW-Cr-7-1200	HW-Cr-14-1200	INC-Cr-14-1200	
Al-Na-limited	BLN-G-129A	HW-AN-7-1200	HW-AN-14-1200	INC-AN-14-1200	
Al-limited	BLM-G-145A	HW-Al-7-1200	HW-Al-14-1200	INC-Al-14-1200	
Bi-limited	BLL-G-46B	HWE-Bi-1200	-	INCE-Bi-1200	Electrical corrosion at 6 amp/inch ² and 1200°C for 3 days
Cr-limited	BLL-G-113A	HWE-Cr-1200	-	INCE-Cr-1200	
Al-Na-limited	BLN-G-129A	HWE-AN-1200	-	INCE-AN-1200	

"-" empty data field

Table 3. Characterization of Inconel 690 Coupons after Standard Glass Contact Corrosion Experiments.

Inconel ID after Corrosion Test	Duration (days)	Temperature (°C)	Half down Loss (mils)	Near Surface (mils)	Scale Development (μm) Spinel Layer in Parenthesis	Scale Structure	Cr Depletion Depth (μm)
INC-Bi-1150	7	1150	0.8	0.6	40 (6)	Continuous (oxide/spinel)	500
INC-Bi-1200	7	1200	2.5	2.5	57 (14)	Continuous (oxide/spinel) with scattered spinel in nearby glass	500
INC-Bi-1230	7	1230	0.9	0.7	57 (14)	Continuous and curved (oxide/spinel) with large spinel crystal	600
INC-Bi-14-1200	14	1200	1.2	4	70 (20)	Continuous and fractured (oxide/spinel)	600
INC-AI-1150	7	1150	1.2	1.5	37 (7)	Continuous and uniform (oxide/spinel)	450
INC-AI-1200	7	1200	0.6	0.9	46 (6, max. 40)	Continuous (oxide/spinel) with irregular pockets of spinel	450
INC-AI-1230	7	1230	<1	NA	60 (15)	Continuous (oxide/spinel) with large spinel crystals	650
INC-AI-14-1200	14	1200	<3	NA	60 (15)	Continuous (oxide/spinel) with large spinel crystals	650
INC-AN-1150	7	1150	<2	NA	40	Continuous, irregular layer of oxide. No spinel layer	350
INC-AN-1200	7	1200	1.2	1.5	55	Continuous, irregular layer of oxide. No spinel layer	350
INC-AN-1230	7	1230	<2	NA	46	Continuous, irregular layer of oxide. No spinel layer	500
INC-AN-14-1200	14	1200	1.6	0	56	Continuous, irregular layer of oxide. No spinel layer	550
INC-Cr-1150	7	1150	1.2	1.4	30	Continuous irregular layer of oxide. No spinel layer. Cr ₂ O ₃ scattered in nearby glass	400
INC-Cr-1200	7	1200	1.2	0.5	45	Continuous irregular layer of oxide. No spinel layer. Cr ₂ O ₃ scattered in nearby glass	450
INC-Cr-1230	7	1230	1.8	0	80	Continuous irregular layer of oxide. No spinel layer. Cr ₂ O ₃ scattered in nearby glass	600
INC-Cr-14-1200	14	1200	1	0.5	70	Continuous irregular layer of oxide. No spinel layer. Cr ₂ O ₃ scattered in nearby glass	600

Table 4a. Glass Composition Before and After Standard Metal Corrosion Tests in Bi-Limited Glass.

Condition	Starting Glass	1150°C, 7-day		1200°C, 7-day		1230°C, 7-day		1200°C, 7-day in 14-day test		1200°C, 14-day	
Analysis	XRF	DCP	XRF	DCP	XRF	DCP	XRF	DCP	XRF	DCP	XRF
Sample ID	BLL-G-46B	HW-Bi-1150M1	HW-Bi-1150	HW-Bi-1200M1	HW-Bi-1200	HW-Bi-1230M1	HW-Bi-1230	HW-Bi-7-1200M1	HW-Bi-7-1200	HW-Bi-14-1200M1	HW-Bi-14-1200
Al ₂ O ₃	11.48	11.65	11.37	12.14	11.58	12.25	11.72	11.28	11.52	11.2	11.56
B ₂ O ₃	11.29	11.30	11.3	10.65	10.65	10.24	10.24	10.61	10.61	11.17	11.17
BaO	0.03	0.03	0.03	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02
Bi ₂ O ₃	6.67	6.97	7.01	6.98	7.01	7.22	6.72	6.52	6.89	6.83	6.74
CaO	0.87	1.01	0.92	1.04	0.95	1.10	0.94	1.00	0.94	1	0.91
Cr ₂ O ₃	0.51	0.21	0.57	0.23	0.52	0.25	0.40	0.26	0.51	0.24	0.48
F	0.49	-	-	-	-	-	-	-	-	-	-
Fe ₂ O ₃	7.38	7.30	7.83	7.60	7.96	7.75	7.82	7.19	7.79	7.51	7.65
K ₂ O	0.54	0.65	0.54	0.60	0.50	0.59	0.49	0.55	0.48	0.59	0.48
Li ₂ O	0.18	0.35	0.35	0.39	0.39	0.38	0.38	0.33	0.33	0.36	0.36
MgO	0.50	0.51	0.49	0.52	0.41	0.52	0.47	0.50	0.51	0.53	0.45
MnO	0.15	0.17	0.16	0.18	0.17	0.18	0.16	0.17	0.17	0.18	0.16
Na ₂ O	15.23	13.58	14.43	13.35	13.79	12.55	14.01	14.00	14.47	14.07	14.37
Nd ₂ O ₃	0.05	-	0.06	-	0.06	-	0.06	-	0.05	-	0.05
NiO	1.67	1.51	1.81	1.66	1.84	1.74	1.76	1.55	1.78	1.6	1.76
P ₂ O ₅	5.06	5.00	5.21	5.08	5.37	4.98	5.46	4.90	5.30	4.69	5.33
PbO	0.30	0.34	0.31	0.33	0.30	0.33	0.29	0.32	0.30	0.34	0.29
SiO ₂	36.27	38.40	36.59	38.12	37.47	38.76	38.09	39.84	37.38	38.69	37.27
SO ₃	0.43	0.08	0.04	0.17	-	0.17	-	-	0.01	-	-
SrO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
TiO ₂	0.19	0.20	0.20	0.20	0.21	0.21	0.21	0.21	0.20	0.21	0.19
ZnO	0.20	0.20	0.21	0.21	0.21	0.20	0.21	0.21	0.21	0.22	0.20
ZrO ₂	0.42	0.47	0.44	0.48	0.46	0.49	0.45	0.48	0.44	0.5	0.44

"-" empty data field

Table 4b. Glass Composition Before and After Standard Metal Corrosion Tests in Cr-Limited Glass.

Condition	Starting Glass	1150°C, 7-day		1200°C, 7-day		1230°C, 7-day		1200°C, 7-day in 14-day test		1200°C, 14-day in 14 day test	
Analysis	XRF	DCP	XRF	DCP	XRF	DCP	XRF	DCP	XRF	DCP	XRF
Sample ID	BLL-G-113A	HW-Cr-1150M1	HW-Cr-1150	HW-Cr1200M1	HW-Cr-1200	HW-Cr-1230M1	HW-Cr-1230	HW-Cr-7-1200M1	HW-Cr-7-1200	HW-Cr-14-1200M1	HW-Cr-14-1200
Al ₂ O ₃	9.07	9.52	9.45	9.69	9.67	9.90	9.82	9.26	9.63	8.98	9.50
B ₂ O ₃	15.88	14.59	14.59	13.66	13.66	13.30	13.3	13.37	13.37	14.15	14.15
BaO	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01
Bi ₂ O ₃	2.90	3.28	2.98	3.25	2.99	3.21	2.96	3.02	3.07	3.04	3.03
CaO	0.83	0.98	0.89	1.02	0.91	0.99	0.94	0.98	0.93	0.95	0.91
Cr ₂ O ₃	1.19	0.65	1.02	0.67	1.01	0.63	0.81	0.61	1.05	0.63	1.07
F	0.49	-	-	-	-	-	-	-	-	-	-
Fe ₂ O ₃	5.06	5.30	5.28	5.35	5.47	5.53	5.53	5.32	5.55	5.37	5.44
K ₂ O	5.53	4.71	4.85	4.32	4.47	4.26	4.39	4.12	4.50	4.39	4.79
Li ₂ O	3.47	3.59	3.59	3.60	3.60	3.35	3.35	3.38	3.38	3.42	3.42
MgO	0.22	0.30	0.26	0.29	0.28	0.29	0.26	0.30	0.27	0.30	0.22
MnO	0.03	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Na ₂ O	7.68	7.23	7.26	6.91	6.91	6.76	6.65	6.61	7.22	6.76	6.93
Nd ₂ O ₃	<0.01	-	0.01	-	0.01	-	0.01	-	0.01	-	-
NiO	0.53	0.59	0.56	0.60	0.58	0.59	0.58	0.60	0.59	0.62	0.62
P ₂ O ₅	1.48	1.44	1.55	1.33	1.56	1.35	1.56	1.21	1.57	1.05	1.56
PbO	0.17	0.20	0.17	0.20	0.17	0.19	0.16	0.18	0.17	0.18	0.17
SiO ₂	44.82	47.19	47.24	48.66	48.4	49.18	49.35	50.71	48.38	49.85	47.89
SO ₃	0.41	0.11	-	0.15	-	0.15	-	-	-	-	-
SrO	<0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.03	0.04	0.03	0.04	0.04	0.04	0.03	0.04	0.04	0.04	0.04
ZnO	0.11	0.11	0.11	0.11	0.11	0.11	0.12	0.12	0.11	0.12	0.11
ZrO ₂	0.07	0.10	0.08	0.09	0.08	0.09	0.08	0.10	0.08	0.09	0.08

"-" empty data field

Table 4c. Glass Composition Before and After Standard Metal Corrosion Tests in Al/Na-Limited Glass.

Condition	Starting Glass	1150°C, 7-day		1200°C, 7-day		1230°C, 7-day		1200°C, 7-day in 14-day test		1200°C, 14-day in 14-day test	
Analysis	XRF	DCP	XRF	DCP	XRF	DCP	XRF	DCP	XRF	DCP	XRF
Sample ID	BLN-G-129A	HW-AN-1150M1	HW-AN-1150	HW-AN-1200M1	HW-AN-1200	HW-AN-1230M1	HW-AN-1230	HW-AN-7-1200M1	HW-AN-7-1200	HW-AN-14-1200M1	HW-AN-14-1200
Al ₂ O ₃	20.74	20.20	20.72	20.65	21.2	20.86	21.56	20.40	21.21	19.82	20.94
B ₂ O ₃	18.29	18.65	18.65	17.54	17.54	17.59	17.59	17.53	17.53	18.43	18.43
BaO	0.07	0.06	0.05	0.06	0.06	0.06	0.06	0.06	0.06	0.05	0.05
Bi ₂ O ₃	1.17	1.42	1.27	1.43	1.27	1.38	1.18	1.25	1.35	1.24	1.20
CaO	1.10	1.34	1.15	1.35	1.20	1.37	1.17	1.25	1.24	1.35	1.16
Cr ₂ O ₃	0.78	0.36	0.73	0.37	0.69	0.34	0.42	0.36	0.72	0.40	0.72
F	0.18	-	-	-	-	-	-	-	-	-	-
Fe ₂ O ₃	3.12	3.27	3.34	3.31	3.45	3.50	3.3	3.30	3.59	3.31	3.36
K ₂ O	0.70	0.79	0.68	0.75	0.64	0.68	0.58	0.69	0.67	0.76	0.62
Li ₂ O	3.58	3.85	3.85	3.76	3.76	3.70	3.7	3.60	3.6	3.70	3.7
MgO	0.26	0.33	0.26	0.32	0.26	0.35	0.26	0.33	0.26	0.35	0.26
MnO	0.05	0.06	0.06	0.06	0.06	0.07	0.06	0.06	0.06	0.06	0.05
Na ₂ O	12.82	11.01	12.27	10.73	11.35	10.46	11.83	11.18	11.21	11.34	12.40
Nd ₂ O ₃	0.01	-	0.01	-	0.01	-	-	-	0.01	-	0.01
NiO	0.16	0.18	0.18	0.18	0.19	0.22	0.18	0.19	0.20	0.20	0.19
P ₂ O ₅	1.99	2.03	2.09	2.10	2.19	2.02	2.16	1.79	2.2	2.26	2.08
PbO	0.10	0.13	0.10	0.13	0.11	0.12	0.09	0.11	0.11	0.11	0.09
SiO ₂	34.17	35.62	34.03	36.57	35.42	36.46	35.29	37.32	35.35	35.96	34.17
SO ₃	0.16	0.10	-	0.10	-	0.18	-	-	-	-	-
SrO	-	0.00	0.00	0.00	-	0.00	-	0.00	0.00	0.00	-
TiO ₂	0.16	0.20	0.18	0.19	0.18	0.20	0.18	0.19	0.19	0.20	0.18
ZnO	0.17	0.15	0.17	0.16	0.19	0.18	0.18	0.18	0.19	0.17	0.18
ZrO ₂	0.20	0.23	0.20	0.22	0.21	0.24	0.20	0.23	0.22	0.25	0.20

"-" empty data field

Table 4d. Glass Composition Before and After Standard Metal Corrosion Tests in Al-Limited Glass.

Condition	Starting Glass	1150°C, 7-day		1200°C, 7-day		1230°C, 7-day		1200°C, 7-day in 14-day test		1200°C, 14-day in 14 day test	
Analysis	XRF	DCP	XRF	DCP	XRF	DCP	XRF	DCP	XRF	DCP	XRF
Sample ID	BLM-G-145A	HW-AI-1150M1	HW-AI-1150	HW-AI-1200M1	HW-AI-1200	HW-AI-1230M1	HW-AI-1230	HW-AI-7-1200M1	HW-AI-7-1200	HW-AI-14-1200M1	HW-AI-14-1200
Al ₂ O ₃	22.29	21.24	21.91	22.42	22.45	21.72	22.36	21.76	22.35	21.12	21.94
B ₂ O ₃	15.20	16.38	16.38	14.95	14.95	15.70	15.70	15.86	15.86	16.74	16.74
BaO	0.32	0.34	0.33	0.34	0.38	0.33	0.35	0.33	0.32	0.35	0.37
Bi ₂ O ₃	1.30	1.41	1.27	1.45	1.30	1.39	1.28	1.31	1.26	1.21	1.25
CaO	5.87	5.80	5.95	5.37	6.14	5.80	6.22	5.52	6.08	5.75	5.99
Cr ₂ O ₃	0.52	0.25	0.53	0.27	0.52	0.25	0.39	0.23	0.50	0.26	0.45
F	0.41		-	-	-	-	-	-	-	-	-
Fe ₂ O ₃	6.16	5.92	6.23	5.76	6.48	6.37	6.52	6.06	6.39	6.18	6.25
K ₂ O	0.42	0.48	0.39	0.50	0.39	0.48	0.37	0.43	0.36	0.47	0.36
Li ₂ O	3.57	3.72	3.72	3.73	3.73	3.45	3.45	3.46	3.46	3.58	3.58
MgO	0.43	0.47	0.41	0.47	0.41	0.45	0.40	0.48	0.35	0.50	0.36
MnO	0.03	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.05	0.04
Na ₂ O	9.80	9.44	9.63	8.48	8.68	8.83	8.58	8.65	8.88	8.76	9.34
Nd ₂ O ₃	0.01		0.01	-	0.01	-	0.01	-	0.01	-	0.01
NiO	0.33	0.30	0.36	0.35	0.40	0.35	0.39	0.34	0.38	0.36	0.37
P ₂ O ₅	1.09	1.05	1.13	1.05	1.21	1.02	1.22	0.93	1.18	1.24	1.14
PbO	0.37	0.41	0.35	0.41	0.35	0.39	0.35	0.39	0.36	0.39	0.36
SiO ₂	31.09	31.87	30.68	33.66	31.85	32.59	31.65	33.44	31.53	32.23	30.82
SO ₃	0.15	0.13	-	0.00	-	0.14	-	-	-	-	-
SrO	-	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-
TiO ₂	0.05	0.04	0.03	0.04	0.04	0.04	0.04	0.04	0.03	0.04	0.03
ZnO	0.09	0.08	0.09	0.08	0.10	0.08	0.09	0.10	0.09	0.08	0.09
ZrO ₂	0.49	0.58	0.50	0.57	0.52	0.55	0.52	0.61	0.50	0.64	0.50

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Table 5. SEM/EDS Analysis of Scale on Inconel 690 (standardless EDS, atomic%) in Bi-Limited Glass at 1150°C, 1200°C, and 1230°C.

Test condition	O	Mg	Al	Ti	Cr	Mn	Fe	Ni	Zn	Sum
1150°C 7-day	55.23	-	0.88	-	18.55	-	12.5	12.28	0.57	100
	55.9	-	-	0.25	42.49	-	1.36	-	-	100
	54.60	-	1.36	0.81	43.23	-	-	-	-	100
	55.08	-	2.07	0.94	41.92	-	-	-	-	100
1200°C 7-day	51.41	0.79	0.75	-	21.53	-	12.3	12.24	0.99	100
	56.42	-	0.65	0.64	42.29	-	-	-	-	100
	56.32	-	0.58	0.23	42.22	-	0.65	-	-	100
1200°C 14-day	39.27	-	-	-	29.07	-	15.7	15.96	-	100
	44.65	-	-	-	55.35	-	-	-	-	100
	45.64	-	-	1.46	52.9	-	-	-	-	100
	44.84	-	-	0.81	54.35	-	-	-	-	100
1230°C 7-day	49.86	0.62	1.04	-	18.7	0.44	14.85	13.96	0.52	100
	54.98	-	-	-	43.89	-	1.14	-	-	100
	55.64	-	0.47	0.3	43.23	-	0.36	-	-	100
	57.97	-	0.99	0.52	40.52	-	-	-	-	100

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Table 6. SEM/EDS Analysis of Scale on Inconel 690 (standardless EDS, atomic%) in Cr-Limited Glass at 1150°C, 1200°C and 1230°C.

-	O	Al	Ti	Cr	Fe	Ni	Sum
1150°C 7-day	56.55	-	-	39.47	3.98	-	100
	55.72	-	-	41.64	2.64	-	100
	55.57	1.26	0.74	42.42	-	-	100
	55.00	-	-	40.09	2.58	2.32	100
1200°C 7-day	56.51	-	-	39.76	3.36	0.37	100
	56.32	-	-	40.18	3.51	-	100
	56.07	-	-	40.39	3.28	-	100
	56.35	0.37	-	43.28	-	-	100
	56.92	-	-	41.77	1.31	-	100
1200°C 14-day	44.56	-	-	55.44	-	-	100
	46.23	-	0.56	53.21	-	-	100
1230°C 7-day	54.05	-	-	41.56	4.39	-	100
	56.16	-	-	43.34	0.5	-	100
	59.92	-	0.5	39.58	-	-	100

"-" empty data field

Table 7. SEM/EDS Analysis of Scale on Inconel 690 (standardless EDS, atomic%) in Al/Na-Limited Glass at 1150°C, 1200°C and 1230°C.

-	O	Mg	Al	Ti	Cr	Fe	Ni	Zn	Sum
1150°C 7-day	52.55	2.37	2.92		29.1	7.06	2.31	3.69	100
	54.22	-	0.98	0.40	43.8	0.61	-	-	100
	53.99	-	1.76	1.17	43.07	-	-	-	100
1200°C 7-day	55.99	-	1.41	-	42.15	0.42	-	-	100
	57.80	-	1.81	0.61	39.78	-	-	-	100
1200°C 14-day	44.50	-	0.98	-	49.55	4.97	-	-	100
	43.06	-	0.83	0.98	55.13	-	-	-	100
1230°C 7-day	54.32	-	2.32	-	40.53	2.82	-	-	100
	54.11	-	2.41	0.18	43.31	-	-	-	100
	55.10	-	1.59	0.44	42.53	0.34	-	-	100

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Table 8. SEM/EDS Analysis of Scale on Surface of Inconel 690 (standardless EDS, atomic%) in Al-Limited Glass at 1150°C, 1200°C and 1230°C.

-	O	Mg	Al	Ti	Cr	Mn	Fe	Ni	Zn	Si	Sum
1150°C 7-day	54.73	-	1.91	0.34	41.58	-	1.44	-	-	-	100
	54.59	-	1.12	0.86	43.43	-	-	-	-	-	100
1200°C 7-day	49.42	1.54	5.26	-	19.41	-	17.2	6.64	0.53	-	100
	54.70	-	1.04	0.23	43.57	-	0.47	-	-	-	100
	53.74	-	1.45	0.75	44.08	-	-	-	-	-	100
1200°C 14-day	46.26	-	3.53	-	20.18	-	21.72	8.31	-	-	100
	46.05	-	3.35	-	22.98	-	19.96	7.65	-	-	100
	45.29	-	1.28	-	52.53	-	0.90	-	-	-	100
1230°C 7-day	53.47	1.60	5.77	-	17.00	-	15.32	5.61	0.69	0.54	100
	56.65	-	1.44	0.27	41.64	-	-	-	-	-	100
	57.27	-	1.11	-	41.62	-	-	-	-	-	100

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Table 9. Characterization of Inconel 690 Coupons after 3-Day Electrical Corrosion Tests.

Inconel ID after corrosion test	Half down loss (mils)	Near surface loss (mils)	Scale development (μm)	Scale structure near half-down	Cr Depletion depth (μm)
INCE-AN-1200	N.A.* ¹	1.1	56	Continuous oxide layer. Absence of spinel	290
INCE-Bi-1200	1.7	0.9	Scale absent* ²	Scale absent* ²	250
INCE-Cr-1200	1.2	1.9	46 (4)	Continuous (oxide/spinel) with scattered spinel in nearby glass	290

*1: Note: the actual diameter at half-down is 1.1 mil larger than the original diameter (0.0770 inch)

*2: Possibly lost during sample preparation

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**Table 10a. Glass Composition Before and After Electrical Corrosion Tests
in Bi-Limited Glass.**

Oxide	Bi limited starting glass BLL-G-46B	1200°C, 3-day electrical corrosion	
		DCP HWE-Bi- 1200M1	XRF HWE-Bi-1200
Al ₂ O ₃	11.48	11.47	11.63
B ₂ O ₃	11.29	11.63	11.63
BaO	0.03	0.02	0.032
Bi ₂ O ₃	6.67	6.26	6.49
CaO	0.87	1.06	0.917
Cl	0.05	-	-
Cr ₂ O ₃	0.51	0.12	0.243
F	0.49	-	-
Fe ₂ O ₃	7.38	6.81	6.64
K ₂ O	0.54	0.58	0.439
Li ₂ O	0.18	0.40	0.4
MgO	0.50	0.54	0.483
MnO	0.15	0.22	0.177
Na ₂ O	15.23	14.15	14.87
Nd ₂ O ₃	0.05	-	0.049
NiO	1.67	2.28	2.21
P ₂ O ₅	5.06	5.20	5.4
PbO	0.30	0.33	0.29
SiO ₂	36.27	37.95	37.19
SO ₃	0.43	-	0.047
TiO ₂	0.19	0.25	0.218
ZnO	0.20	0.17	0.157
ZrO ₂	0.42	0.52	0.417

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**Table 10b. Glass Composition Before and After Electrical Corrosion Tests
in Cr-Limited Glass.**

Oxide	Cr-limited starting glass BLL-G-113A	1200°C, 3-day electrical corrosion	
		DCP HWE-CR- 1200M1	XRF HWE-Cr-1200
Al ₂ O ₃	9.07	9.38	9.5
B ₂ O ₃	15.88	15.22	15.22
BaO	0.02	0.01	0.016
Bi ₂ O ₃	2.90	1.74	1.63
CaO	0.83	1.01	0.852
Cl	-	-	-
Cr ₂ O ₃	1.19	0.22	0.597
F	0.49	-	-
Fe ₂ O ₃	5.06	5.08	4.9
K ₂ O	5.53	4.51	4.87
Li ₂ O	3.47	3.88	3.88
MgO	0.22	0.27	0.247
MnO	0.03	0.07	0.052
Na ₂ O	7.68	7.10	8.02
Nd ₂ O ₃	<0.01	-	-
NiO	0.53	3.31	3.33
P ₂ O ₅	1.48	1.54	1.5
PbO	0.17	0.17	0.159
SiO ₂	44.82	46.23	44.92
SO ₃	0.41	-	0.03
TiO ₂	0.03	0.07	0.061
ZnO	0.11	0.07	0.064
ZrO ₂	0.07	0.09	0.071

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**Table 10c. Glass Composition Before and After Electrical Corrosion Tests
in Al/Na-Limited Glass.**

Oxide	Al-Na limited starting glass	1200°C, 3-day electrical corrosion	
		DCP	XRF
	BLN-G-129A	HWE-AN- 1200M1	HWE-AN-1200
Al ₂ O ₃	20.74	19.68	20.94
B ₂ O ₃	18.29	18.63	18.63
BaO	0.07	0.05	0.047
Bi ₂ O ₃	1.17	1.24	1.1
CaO	1.10	1.34	1.16
Cl	-	-	-
Cr ₂ O ₃	0.78	0.09	0.188
F	0.18	-	-
Fe ₂ O ₃	3.12	2.91	2.93
K ₂ O	0.70	0.74	0.621
Li ₂ O	3.58	3.73	3.73
MgO	0.26	0.29	0.199
MnO	0.05	0.08	0.071
Na ₂ O	12.82	11.32	12.51
Nd ₂ O ₃	0.01	-	0.013
NiO	0.16	1.20	1.2
P ₂ O ₅	1.99	2.16	2.1
PbO	0.10	0.11	0.1
SiO ₂	34.17	35.81	33.89
SO ₃	0.16	-	0.032
TiO ₂	0.16	0.25	0.211
ZnO	0.17	0.09	0.091
ZrO ₂	0.20	0.24	0.187

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**Table 11. Composition of Scale on Surface Inconel 690 in Bi-Limited Glass After 3 Days
Electrical Corrosion (atomic % by SEM/EDS).**

a) Near glass surface

Spectrum	O	Mg	Al	Ti	Cr	Fe	Ni	Total
Spectrum 1	40.18	-	1.34	1.6	56.88	-	-	100
Spectrum 2	37.43	-	1.75	1.38	59.44	-	-	100
Spectrum 3	33.53	-	11.03	16.69	12.78	3.99	21.99	100
Spectrum 5	36.58	-	5.42	5.86	43.00	1.37	7.78	100
Spectrum 7	58.54	20.69	-	20.76	-	-	-	100

b) Half-down

Spectrum	O	Mg	Al	Ti	Cr	Fe	Ni	Total
Spectrum 3	26.47	-	-	1.24	34.45	7.01	30.83	100
Spectrum 4	42.29	-	0.70	1.26	54.66	-	1.10	100

c) Near bottom

Spectrum	O	Mg	Al	Ti	Cr	Fe	Ni	Total
Spectrum 1	40.74	-	1.48	0.95	55.95	-	0.88	100
Spectrum 2	39.2	-	2.56	1.29	56.95	-	-	100
Spectrum 3	31.34	-	3.33	1.18	53.82	2.39	7.94	100
Spectrum 4	44.58	-	10.81	22.9	15.53	-	6.18	100
Spectrum 5	45.02	-	2.91	43.19	4.84	-	4.04	100

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Table 12. Composition of Scale on Inconel 690 in Cr-Limited Glass After 3 Days Electrical Corrosion (SEM/EDS, atomic %).

a) Near glass surface

Spectrum	O	Al	Ti	Cr	Fe	Ni	Total
Spectrum 1	38.98	-	-	39.61	6.51	14.73	100
Spectrum 2	42.87	-	0.52	56.61	-	-	100
Spectrum 3	45.97	-	1.26	52.41	-	-	100
Spectrum 4	38.30	3.62	5.32	51.54	-	1.21	100

b) Half-down

Spectrum	O	Al	Ti	Cr	Fe	Ni	Total
Spectrum 2	36.46	-	-	41.42	6.61	15.51	100
Spectrum 3	39.66	1.31	-	59.03	-	-	100

c) Near bottom

Spectrum	O	Al	Ti	Cr	Fe	Ni	Total
Spectrum 2	38.82	1.08	-	39.07	6.99	14.05	100
Spectrum 3	38.15	1.02	-	42.71	5.92	12.18	100
Spectrum 4	43.31	-	1.00	55.70	-	-	100
Spectrum 5	44.25	7.24	10.07	37.63	-	0.81	100

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Table 13. Composition of Scale on Inconel 690 in Al/Na-Limited Glass After 3 Days Electrical Corrosion (SEM/EDS, atomic %).

a) Near glass surface

Spectrum	O	Al	Ti	Cr	Mn	Fe	Ni	Zn	Total
Spectrum 2	43.58	1.55	-	33.37	-	9.05	11.81	0.03	100
Spectrum 3	42.95	2.04	-	31.87	-	10.25	12.82	0.07	100
Spectrum 4	47.09	-	0.30	51.71	-	0.62	-	-	100
Spectrum 5	44.72	0.61	1.14	52.41	-	-	1.12	-	100

b) Half-down

Spectrum	O	Al	Ti	Cr	Mn	Fe	Ni	Zn	Total
Spectrum 2	43.03	1.84	-	33.83	0.78	7.77	12.44	0.32	100
Spectrum 3	43.76	2.89	-	30.49	-	9.30	13.42	0.13	100
Spectrum 4	44.36	1.13	0.68	52.4	0.77	-	0.66	-	100
Spectrum 5	45.38	2.25	-	33.73	0.63	6.15	10.4	0.19	99
Spectrum 6	43.98	1.74	-	37.42	-	5.94	10.62	0.29	100
Spectrum 7	45.05	0.39	0.23	53.92	-	0.41	-	-	100
Spectrum 8	44.10	-	1.05	54.06	-	-	0.80	-	100

c) Near bottom

Spectrum	O	Al	Ti	Cr	Mn	Fe	Ni	Zn	Total
Spectrum 2	46.36	2.09	-	32.74	-	7.73	10.65	0.42	100
Spectrum 3	43.8	2.47	-	36.04	-	6.81	10.87	-	100
Spectrum 4	44.64	2.05	-	51.24	-	0.88	1.19	-	100
Spectrum 5	45.56	3.46	1.07	49.91	-	-	-	-	100

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Figure 1. Schematic diagram of a metal coupon showing typical dimensions and line indicating where the coupon is sectioned after testing.

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Figure 2. Experimental set up for standard metal corrosion tests.

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Figure 3. Test setup for the electrical corrosion experiments.

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Figure 4. Circuit for the electrical metal corrosion tests.

a) 1150°C

b) 1200°C

c) 1230°C

Figure 5. Scale on Inconel 690 coupon after 7 days in Bi-limited glass.

Figure 6. Internal structural damage in Inconel 690 near half-down region after 7 days in Bi-limited glass.

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Figure 7. Cr depletion inside Inconel 690 coupon (SEM/EDS line scan and point analysis overlay) in the Bi-limited glass. X-axis plots the distance from the remaining metal surface; Y-axis plots the atomic % of Cr.

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c)

c) 1230°C

Figure 7 (continued). Cr depletion inside Inconel 690 coupon (SEM/EDS line scan and point analysis overlay) in the Bi-limited glass. X-axis plots the distance from the remaining metal surface; Y-axis plots the atomic % of Cr.

Figure 8. Inconel 690 coupon after 14 days in Bi-limited glass: a) Scale (SEM image); b) Internal structural damage (SEM image); c) Cr depletion (line scan by SEM/EDS).

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**Figure 8d. Large scale SEM image of Inconel 690 coupon after 14 days in Bi-limited glass.
Cross section through the glass contact surface is on the left.**

Figure 9. Scale on Inconel 690 coupon after 7 days in Cr-limited glass.

Figure 10. Internal structural damage in Inconel 690 near half-down region after 7 days in the Cr-limited glass.

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Figure 11. Cr depletion inside Inconel 690 coupon (SEM/EDS line scan and point analysis overlay) in the Cr-limited glass. X-axis plots the distance from the remaining metal surface; Y-axis plots the atomic % of Cr.

a) Scale

b) Internal structural damage

c) Cr depletion

Figure 12. Inconel 690 coupon after 14 days at 1200°C in Cr-limited glass: a) Scale (SEM image); b) Internal structural damage (SEM image); c) Cr depletion (SEM/EDS line scan).

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**Figure 12d. Large scale SEM image of Inconel 690 coupon after 14 days in Cr-limited glass.
Cross section through the glass contact surface is on the left.**

a) 1150°C

b) 1200°C

c) 1230°C

Figure 13. Scale on Inconel 690 coupon after 7 days in Al/Na-limited glass.

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a) 1150°C

b) 1200°C

c) 1230°C

Figure 14. Internal structural damage in Inconel 690 near half-down region after 7 days in the Al/Na-limited glass.

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Figure 15. Cr depletion inside Inconel 690 coupon (SEM/EDS line scan and point analysis overlay) in the Al/Na-limited glass. X-axis plots the distance from the remaining metal surface; Y-axis plots the atomic % of Cr.

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Figure 15 (continued). Cr depletion inside Inconel 690 coupon (SEM/EDS line scan and point analysis overlay) in the Al/Na-limited glass. X-axis plots the distance from the remaining metal surface; Y-axis plots the atomic % of Cr.

a) Scale

b) Internal structural damage

c) Cr depletion

Figure 16. Inconel coupon after 14 days at 1200°C in Al/Na-limited glass: a) Scale (SEM image); b) Internal structural damage (SEM image); c) Cr depletion (SEM/EDS line scan).

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Figure 16d. Large scale SEM image of Inconel 690 coupon after 14 days in Al/Na-limited glass. Cross section through the glass contact surface is on the left.

a) 1150°C

b) 1200°C

c) 1230°C

Figure 17. Scale on Inconel 690 coupon after 7 days in Al-limited glass.

a) 1150°C

b) 1200°C

c) 1230°C

Figure 18. Internal structural damage in Inconel 690 near half-down region after 7 days in Al-limited glass.

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Figure 19. Cr depletion inside Inconel 690 coupon (SEM/EDS line scan and point analysis overlay) in the Al-limited glass. X-axis plots the distance from the remaining metal surface; Y-axis plots the atomic % of Cr.

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Figure 19 (continued). Cr depletion inside Inconel 690 coupon (SEM/EDS line scan and point analysis overlay) in the Al-limited glass. X-axis plots the distance from the remaining metal surface; Y-axis plots the atomic % of Cr.

Figure 20. Inconel coupon after 14 days at 1200°C in Al-limited glass: a) Scale (SEM image); b) Internal structural damage (SEM image); c) Cr depletion (SEM/EDS line scan).

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**Figure 20d. Large scale SEM image of Inconel 690 coupon after 14 days in Al-limited glass.
Cross section through the glass contact surface is on the left.**

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a) Near glass surface

b) Half down

c) Near bottom

Figure 21. Cross sections (SEM images) of Inconel 690 pin after 3 days electrical corrosion in Bi-limited glass at 1200°C.

a) Near glass surface

b) Half down

c) Near bottom

Figure 21. Cross sections (SEM images) of Inconel 690 pin after 3 days electrical corrosion in Bi-limited glass at 1200°C.

Figure 23. Cross sections (SEM images) of Inconel 690 pin after 3 days electrical corrosion in Al/Na-limited glass at 1200°C.

Figure 24. Cross sections (SEM images) of Inconel 690 pin after 3 days electrical corrosion in Bi-limited glass at 1200°C.

a) Near glass surface

b) Half down

c) Near bottom

Figure 25. Cross sections (SEM images) of Inconel 690 pin after 3 days electrical corrosion in Cr-limited glass at 1200°C.

Figure 26. Cross sections (SEM images) of Inconel 690 pin after 3 days electrical corrosion in Al/Na-limited glass at 1200°C.

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Figure 27. Cr depletion inside Inconel 690 pins at half-down after 3 days electrical corrosion (SEM/EDS line scans): a) Bi-limited glass; b) Cr-limited glass; and c) Al/Na-limited glass.

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Figure 27 (continued). Cr depletion inside Inconel 690 pins at half-down after 3 days electrical corrosion (SEM/EDS line scan): a) Bi-limited glass; b) Cr-limited glass; and c) Al/Na-limited glass.

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Figure 28. Correlation between the depth of Cr-depletion inside the Inconel 690 coupons and the thickness of the metal scale. Data points include all standard metal corrosion test results at three different temperatures.

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Figure 29. Cr-depletion depth inside Inconel 690 coupons at temperatures of 1150, 1200, and 1230°C (measured near half-down region by SEM/EDS).

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Figure 30. Progress of Cr-depletion inside Inconel 690 versus corrosion test duration. Points are from Inconel 690 coupon corrosion experiments at 1200°C for 3, 7, and 14 days for four glasses. The lines are from regression equations for depletion depth proportional to the square root of the test time.

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APPENDIX A

Inconel 690 Corrosion Test with LAW Iron Phosphate Glass

Internal VSL Report

Inconel 690 Corrosion Test with LAW Iron Phosphate Glass

12/2002-1/2003

Alloy: Inconel 690, test coupon dimensions: 0.15" X 0.3" X 1.5";

Glass: 60g of DAY-LAW-1-1 glass;

Test set up: Standard static glass contact corrosion test in 50ml Pt crucible;

Test duration: 3 days;

Test temperature: 1130°C.

I. Visual inspection of test coupon

After three days, the metal coupon in contact with the molten phosphate glass was severely corroded, as also was the material in the vapor phase above glass line. The scale that developed on the alloy exposed to glass vapor was greatly expanded and showed signs of blistering and spalling (Figure 1).

Figure 1

The cross-section of the reacted coupon (embedded in epoxy), shown in Figure 2, reveals that the alloy in contact with molten phosphate glass was severely damaged. Dimension loss at the neck and half-down region (as indicated in Figure 2) is vastly greater than the typical corrosion loss of Inconel 690 in contact with borosilicate melts. A large number of alloy fragments are observed floating near the surface of the remnant coupon.

Figure 2

II Dimensional loss

The corrosion damage of an engineering alloy is commonly characterized by the dimension loss of the reacted coupon in a representative test environment. An optical microscope was used to measure the width of the reacted coupon at different locations before and after the corrosion test. For comparison, it is noted that the typical dimension loss under the same test conditions but longer duration (7 days rather than 3 days here) is less than 1-2 mil for borosilicate waste glasses. Table 1 lists the measured dimensional loss for the different regions of the reacted coupon. The neck region, where the coupon is in contact with both glass and vapor, has the largest dimension loss. The region above the neck has suffered the least, yet still considerably large dimension loss. The half-down region, the midpoint between the neck and the bottom end of the coupon, and the bottom end of the coupon have dimension losses similar to neck loss. The average corrosion rate in the three day test is about 10 mil/day (~250 microns/day).

Table 1

	Measured width [inch]	Dimensional loss [mil]
Original	0.151	-
Above the neck	0.132	9
At the neck	0.092	29
Half down	0.106	23
Bottom end of the coupon	0.099	26

III Microscopic Examination by SEM/EDS

Complementary to the dimension loss data, microscopic examination of metal test coupons provides information about the nature of the corrosion damage and the structural alteration or degradation inside the metal, which are important for a comprehensive assessment of corrosion damage and the engineering value of a proposed alloy material. Scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDS) was used to characterize the microstructure and chemical composition of the Inconel 690 coupon after the test.

Glass-metal contact region:

The damage of Inconel 690 alloy in this region is most evident in the metal loss and excessive scale development. Figure 3 shows an SEM image of the scale

Figure 3

formed on the metal surface (note: the bright region at the right side of the image is the alloy, the majority of the grey areas of different shades are the scale with the infiltrated glass). In some regions as thick as 1.2 mm, the scale has a complicated structure, consisting mostly of Cr and P. The excessive scale formation and the high chromium content would inevitably deplete Cr from the interior of the alloy, which in turn tends to

facilitate further corrosion. Indeed, the EDS line-scan shows substantial Cr depletion 200 microns deep inside the alloy (Figure 4).

Figure 4

However, beyond the Cr depleted region, there is no clear sign of additional inter-granular damage that is often present in the Inconel 690 alloy in contact with the borosilicate melts, which shows much lower dimensional losses. In addition to the Cr-P compound, large metal-like fragments of Ni and P are observed near the remnants of the alloy coupon (Figure 5 and Figure 6).

Figure 5

Figure 6

Vapor-metal contact region:

The damage of the Inconel 690 coupon above the surface of the phosphate melt is remarkably extensive when compared to the typical extent of degradation of Inconel 690 exposed to hot air at the same temperature. A thick layer of oxide scale (about 500 μm), denser than that in the glass-contact region, formed on the metal surface (Figure 7) containing mainly chromium oxide plus oxides of iron, aluminum, and small amounts of titanium and nickel (Figure 8). On the top of the chromium oxide layer is a more or less continuous layer (about 50 μm) of Ni oxide and likely Ni-Fe-Al spinel with small amounts of Cr (Figure 7 and Figure 9).

Figure 7

Figure 8

Figure 9

It is worth noting that the characteristic spinel phase formed on the Inconel 690 above the borosilicate melts at the same test temperature is rich in Cr_2O_3 . It seems that the presence of phosphorus in the phosphate glass influenced the nature of the scale formation in the vapor contact region. It is probably not coincidental that phosphorus was identified within the grain boundaries deep inside the alloy (Figures 10 and 11). Moreover, the grain size of the Inconel 690 deep inside the coupon (far from the surface) had enlarged to 300 to 400 μm accompanied by clear signs of grain boundary damage (Figure 10). As shown in Figure 12, the inter-granular attack involving phosphorus and the enormously enlarged grain size reaches to 1000 μm from the metal surface.

Figure 10 **Figure 11**

Figure 12

Such grain growth and inter-granular attack are typically associated with weakening and embrittlement of the alloy and such factors must be carefully considered in addition to the simple dimensional loss from the coupon.