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Literature Review: Assessment of DWPF Melter and Melter Off-gas System Lifetime

M. M. Reigel

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EXECUTIVE SUMMARY

A glass melter for use in processing radioactive waste is a challenging environment for the materials of construction (MOC) resulting from a combination of high temperatures, chemical attack, and erosion/corrosion; therefore, highly engineered materials must be selected for this application. The focus of this report is to review the testing and evaluations used in the selection of the Defense Waste Processing Facility (DWPF), glass contact MOC specifically the Monofrax® K-3 refractory and Inconel® 690 alloy. The degradation or corrosion mechanisms of these materials during pilot scale testing and in-service operation were analyzed over a range of oxidizing and reducing flowsheets; however, DWPF has primarily processed a reducing flowsheet (i.e., $Fe^{2+}/\Sigma Fe$ of 0.09 to 0.33) since the start of radioactive operations. This report also discusses the materials selection for the DWPF off-gas system and the corrosion evaluation of these materials during pilot scale testing and non-radioactive operations of DWPF Melter #1. Inspection of the off-gas components has not been performed during radioactive operations with the exception of maintenance because of plugging.

Development of the current DWPF glass melter configuration dates back to 1976, when work began on the first prototype melter system. From 1976 – 1994, five pilot scale melters were tested to verify and improve the design of the DWPF Melter and off-gas system. During that time, several bench-top, crucible, and laboratory scale tests of the two main glass contact materials, Monofrax® K-3 refractory and Inconel® 690 alloy for glass contact (e.g. electrodes, riser, pour spout, and drain valve) and top-head components, were performed. Results of the laboratory coupon tests indicated the lifetime of the DWPF Melter was limited by the refractory corrosion. Based on these crucible scale tests, the expected melter lifetime was approximately 2 – 6 years at the melt line where maximum corrosion was observed. The pilot-scale melter testing confirmed that a two year melter life was adequate and results indicated the lifetime could be extended past the two year design basis. The literature suggests the two year melter lifetime was originally based on the average lifetime of commercial fiberglass melters at the time which also used Monofrax® K-3 refractory but at higher temperatures than the DWPF nominal temperature of 1150 °C.

Extensive laboratory and scaled melter tests were performed in order to rank and ultimately select Inconel® 690, Hastelloy® C-276, Allvac® Allcorr®, and Type 304L stainless steel for the DWPF off-gas system components. The results of the off-gas coupon tests were confirmed by the corrosion evaluation of the Integrated DWPF Melter System (IDMS) as well as melter off-gas inspections after the DWPF Melter #1 non-radioactive runs. Although there have been several pluggages of the DWPF melter off-gas system during radioactive operations from sulfate, chloride, and glass accumulations, corrosion has not limited the lifetime of the off-gas components. To date, the original off-gas components for the DWPF melter are still in operation, indicating their design life of up to five years is overly conservative.

Various degrees of degradation were observed on the DWPF Melter #1 Inconel® 690 top-head components during the non-radioactive DWPF startup operation, with the most severe attack occurring in the regions of the melter vapor space and off-gas system that ranged between 500 and 800 °C. This attack was attributed to chloride and sulfate bearing compounds present in the off-gas condensing and concentrating on the colder regions of the top head and off-gas components; thus breaking down the protective chromium oxide layer of the Inconel® 690. Removal of the protective layer allows low melting point salt compounds to penetrate further into the metal substrate resulting in accelerated metal wastage rates. Prior to radioactive operations of Melter #1, the most susceptible Inconel® 690 components were altered by a weld overlay to extend their lifetime. For the Monofrax® K-3 refractory, both non-radioactive and radioactive operations of Melter #1 confirmed the results of the pilot-scale melter testing showing the area of highest refractory wear is at or slightly below the normal melt line. DWPF Melter #1 was shut down after eight years of total operation from the combination of an extended DWPF outage and the failure of a dome (lid) heater. Melter #1 was not shut down because of corrosion of the melter MOC; in

fact, the Monofrax® K-3 refractory and Inconel® 690 components showed minimal wear, indicating the melter lifetime was not limited by these MOC. DWPF Melter #2 continues to operate after 11 years, further reinforcing that the two year design basis for DWPF Melters is overly conservative.

Testing to date for the MOC for the Hanford Waste Treatment and Immobilization Plant (WTP) melters is being reviewed with the lessons learned from DWPF in mind and with consideration to the changes in the flowsheet/feed compositions that have occurred since the original testing was performed. This information will be presented in a separate technical report that identifies any potential gaps for WTP processing.

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LIST OF ABBREVIATIONS

BU	Backup
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
HEME	High Efficiency Mist Eliminator
HEPA	High Efficiency Particulate Air
HLW	High-level waste
HSS	Hydro-sonic® Scrubber
IDMS	Integrated DWPF Melter System
LAW	Low-activity waste
LSFM	Large Slurry Fed Melter
MOC	Material(s) of Construction
MOG	Melter Off-Gas
OCF	Owens-Corning Fiberglas
OGC	Off-Gas Condenser
OGCT	Off-Gas Condensate Tank
OGFC	Off-Gas Film Cooler
ORP	Office of River Protection
PNL	Pacific Northwest Laboratory
PNNL	Pacific Northwest National Laboratory
REDOX	REDuction/OXidation
SAS	Steam Atomized Scrubber
SCM	Small Cylindrical Melter
SEM	Scanning Electron Microscopy
SGM	Scale Glass Melter
SRL	Savannah River Laboratory
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SS	Stainless Steel
SCFH	Standard Cubic Feet per Hour
TDS	Technical Data Summary
TTQAP	Task Technical and Quality Assurance Plan
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	X-ray Diffraction

1.0 Introduction

The U.S. Department of Energy's (DOE) contractor, Bechtel National Incorporated, is building the Hanford Tank Waste Treatment and Immobilization Plant (WTP) at the Hanford Site in Washington to remediate roughly 55 million gallons of high-level radioactive waste (HLW) that is being stored in 177 underground tanks. The plan is to separate the radioactive waste into HLW and low-activity waste (LAW) fractions that will then be vitrified in stable borosilicate glass with Joule-heated ceramic melters. Efforts are being made to increase the loading of Hanford tank wastes in glass while meeting melter throughput and lifetime expectancies, as well as requirements for processing, regulatory compliance, and product quality. To achieve these goals, the DOE – Office of River Protection (DOE-ORP) has requested that the Savannah River National Laboratory (SRNL) support the advancement of glass formulations and process control strategies in various key technical areas, as defined in the Task Technical and Quality Assurance Plan (TTQAP).[1] The focus of this report is a literature review detailing the corrosion evaluation of melter materials, both glass contact materials and off-gas components, performed for the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS). Information from this report will be used as part of the effort to determine whether there are any gaps in the WTP melter and off-gas testing to date or potential improvements to the system that come from knowledge gained from 18 years of radioactive melter operations at the SRS DWPF.

A glass melter intended for use in processing radioactive waste is a challenging environment for the materials of construction (MOC) resulting from the combination of high temperatures, chemical attack, and erosion/corrosion; therefore, highly engineered materials must be selected for this application.[1] Corrosive species loading in the glass melt can attack the glass contact MOC and limit the useful lifetime of these materials, leading to a limited operational lifetime of the HLW melters. These species, such as nitrates, halides, sulfates, and phosphates, corrode the melter MOC while halides, sulfates, and phosphates also limit the waste loading in the glass. Additionally, glass processing properties such as low viscosity[2-4] and the reduction/oxidation (REDOX) chemistry of the glass melt affect the corrosion rate of glass contact materials.[5-8] The focus of this report is to review the laboratory testing and pilot scale melter tests used in the selection of the MOC of the DWPF Melter, specifically the Monofrax® K-3 refractory and Inconel® 690 alloy*, as well as the durability (corrosion resistance) of the melter off-gas (MOG) components. The degradation or corrosion mechanisms of these materials during pilot-scale melter testing and in-service operation will be reviewed across a range of oxidizing and reducing melt conditions. Throughout this document, including DWPF operations as well as scaled melter testing, an oxidizing feed is defined as having an $Fe^{2+}/\Sigma Fe$ ratio of <0.09, a reducing feed is defined as having an $Fe^{2+}/\Sigma Fe$ ratio of 0.09 – 0.33, and an overly reduced feed is defined as having an $Fe^{2+}/\Sigma Fe$ ratio of >0.33. These limits were defined in Reference 9 based on the Fe^{2+}/Fe^{3+} ratio and converted to $Fe^{2+}/\Sigma Fe$ ratio. The lower limit of the reducing feed is to prevent foaming while the upper limit prevents metal and sulfide formation in the melter.

At the SRS, the DWPF has completed more than 18 years of radioactive operations. Lessons learned regarding corrosion of melter materials and off-gas components from operating DWPF Melters #1 and #2, as well as the pilot scale melters at SRS, will be summarized in this document. The pilot scale melters were built and tested in order to verify and improve the design of the DWPF production melter.[10-13] Extensive testing of MOG MOC and components was performed to verify operation and functionality under in-service conditions.[10,13-17] The predicted lifetime of the off-gas system as well as Melters #1 and #2 will be compared to the in-service lifetime to determine whether the lifetime prediction is overly conservative.

* Monofrax® K-3 is a registered trade mark of the Carborundum Company and Inconel® 690 is a registered trademark of the Special Metals.

1.1 Quality Assurance

This review is performed as part of a TTQAP.[1] Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. The SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

2.0 Background

The DWPF Melter was designed to immobilize, thru vitrification, radioactive waste stored as liquids at the DOE SRS. The full scale DWPF melter is cylindrical with a 28 ft^2 glass melt pool surface area and a melt volume of about 78 ft^3.[10] It is a refractory-lined, joule-heated, slurry-fed melter which is encased in a water-cooled 304L stainless steel (SS) shell.[10] Before the DWPF Melter was designed, testing of the two main glass contact materials that impact melter life (Monofrax® K-3 refractory and Inconel® 690 alloy) was performed.[3,4,18] In addition, design of the MOG system and selection of its MOC (Inconel® 690, Hastelloy® C-276, Allvac® Allcorr®, and Type 304L SS) began in late 1970's.

Development of the current DWPF glass melter configuration dates back to 1976, when work began on the first prototype melter system with calcine feeding.[10] From 1976 – 1994, five pilot scale melters were tested to verify and improve the design of the DWPF Melter and off-gas system.[10-13,19,20] An additional goal of the pilot scale melters was to satisfy the final phase of the Melter Materials Compatibility Program which was to perform simulated service tests to determine MOC wear rates in actual melter environments. A timeline of melter operations at SRS is shown in Table 2-1.

Table 2-1. Melter operation timeline at SRS.

Date	Event
~ 1977	MOC Coupon testing began
1978-1981	Large Scale Project 1941 Melter Testing
1979-1982	Small Cylindrical Melter (SCM) Testing
1982-1985	Large Slurry Fed Melter (LSFM) Testing
1986-1988	Scale Glass Melter (SGM) Testing
1988-1995	Integrated DWPF Melter System (IDMS) Testing
April 1994	Melter #1 began non-radioactive operations
March 1996	Melter #1 began radioactive operations
Nov 2002	Melter #1 shutdown
March 2003	Melter #2 began radioactive operations
Sept 2010	Bubblers installed in Melter 2
Present	Melter #2 continues to operate

2.1 DWPF Melter Design Overview

The DWPF Melter (Figure 2-1) is currently one of the largest operating HLW melters in the world and is designed to immobilize high-level radioactive waste by converting it into a stable borosilicate glass.[10] It has a 28 ft^2 glass melt pool surface area and a melt volume of about 78 ft^3. It is a refractory-lined, joule-heated, slurry-fed melter which is encased in a water-cooled Type 304L SS shell. The inside of the DWPF Melter is cylindrical (geometrically round) to prevent refractory cave-in[13] and maximize natural convection. The cylindrical design also prevents cold melter corners that can occur in square or oblong melters without additional convection. The DWPF Melter has two pairs of diametrically opposed

Inconel® 690 electrodes and the glass contact refractory is 12 inch thick fused-cast Monofrax® K-3 (Figure 2-2).[10,13]

The DWPF Melter also has two sets of Inconel® 690 plenum (dome) heaters, four dome heaters per set, that supply additional heat energy above the melt pool (Figure 2-3).[10,13] These heaters are 3 inch diameter tubes that are resistance heated to aid in increasing melting rate, melt start-up frit and to elevate the plenum temperature to assist in conversion of volatile species. The DWPF Melter glass pool is maintained between 1050 °C and about 1175 °C.[12] The maximum temperature of the melt pool, riser heater, and pour spout heater is 1200 °C in order to protect the Inconel® 690 components, including the electrodes.[12,21] The effect of melter operating temperature relative to Inconel® 690 components is discussed in sections 2.2 and 2.4.1. Molten glass is poured via differential pressure through an Inconel® 690 lined riser and pour spout and into SS canisters.[10] Both the riser and pour spout use resistance heated serpentine Inconel® 690 heaters.[13] A heated bellows connects the 10 foot tall by 2 foot diameter SS canisters to the pour spout.[13] Note that the bellows was not heated in Melter #1 and a nickel liner was used to shed glass. The bellows were heated in Melter #2 and the nickel liner is still in use. The melter also has a drain valve that is designed to be only used at the end of the life of the melter to remove as much glass as possible from the melter before it is shut down and replaced.[13] Operation of Melter #1, including shutdown inspections, is further discussed in section 5.1 and Melter #2 is discussed in section 5.2. Further details on the DWPF Melter design can be found in literature.[10,12,13,21]

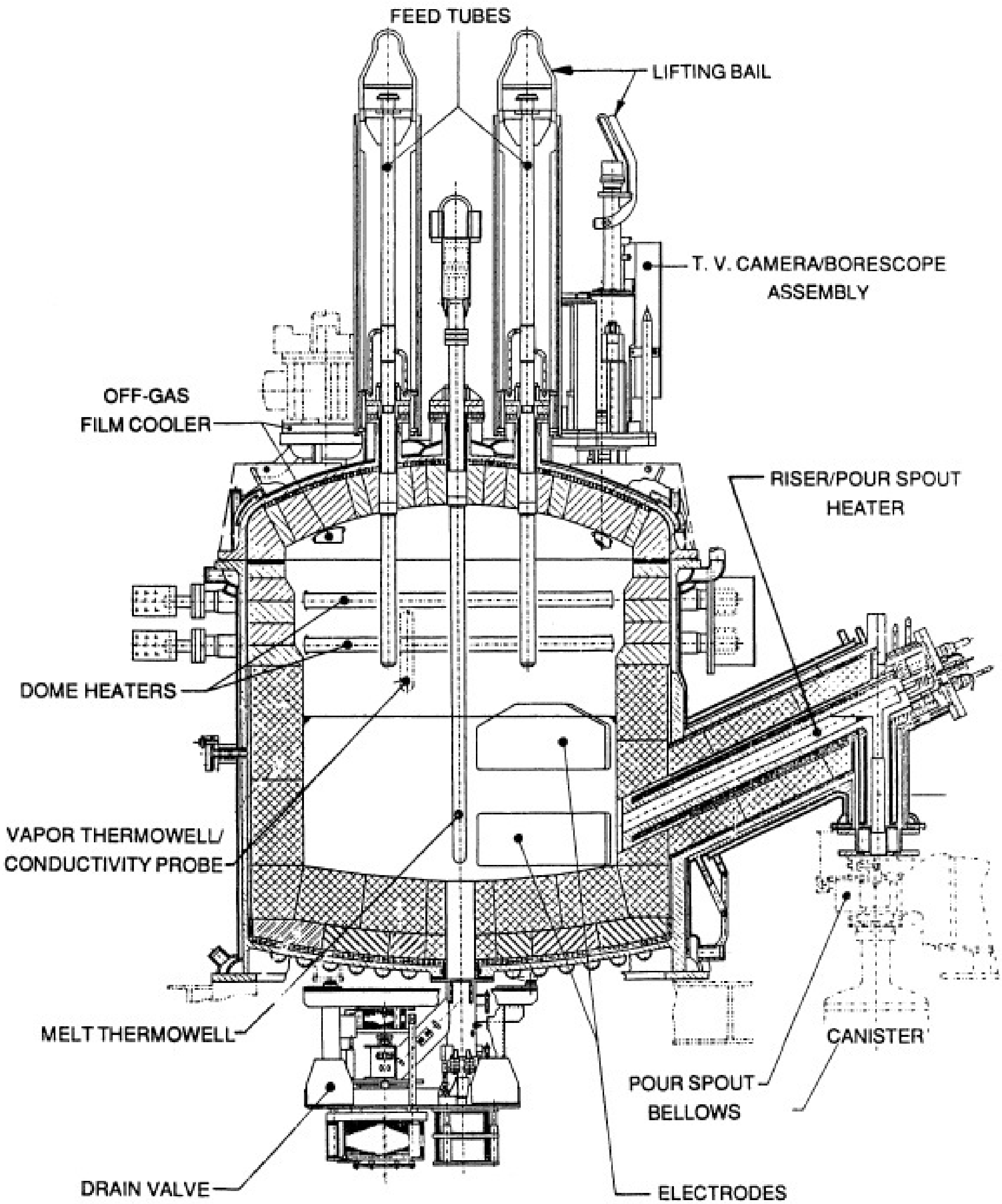

Figure 2-1. Cross-sectional view of DWPF Melter (prior to addition of bubblers).[10]

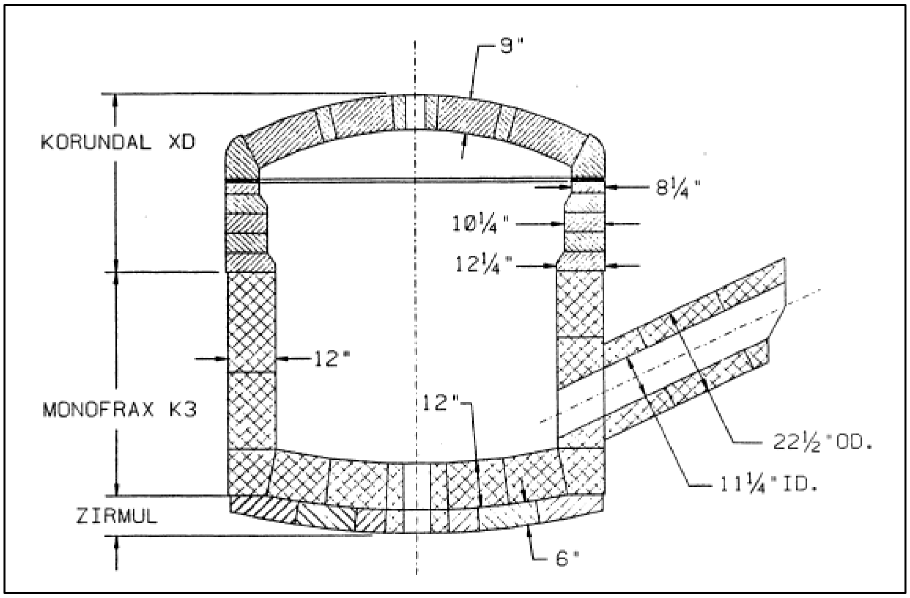

Figure 2-2. DWPF Melter Refractory.[10]

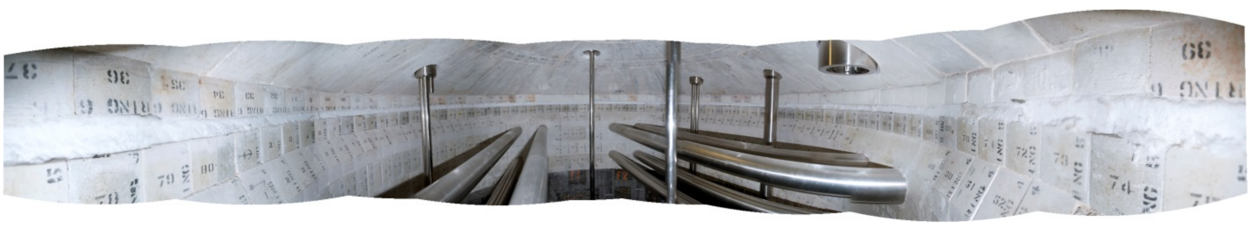

Figure 2-3. Photograph of the DWPF Melter dome heaters. Note: photo was taken with a wide angle lens so heaters appear curved.

2.2 Glass Contact Materials

The Nuclear Materials Division of Savannah River Laboratory (SRL) developed the Melter Materials Compatibility Program during 1977.[18] The goal of this program was to evaluate the corrosion/erosion resistance of melter glass contact materials, and subsequently, to recommend electrode and refractory candidates for use in the joule-heated ceramic melter.[3] The experimental program consisted of three phases: laboratory scale “finger tests” under static and dynamic conditions in simulant waste glass, “finger tests” in actual radioactive waste, and finally, “simulated service test” to evaluate the performance of the MOC.[3,4,18] Results of the materials testing as they relate to the determination of the DWPF Melter lifetime are discussed in section 6.0. In addition to erosion/corrosion resistance, the final selection of materials for the electrode and refractory components was based on the materials’ electrical resistivity, thermal shock resistance, thermal expansion and conductivity, cost, and availability.[3] Based on these criteria and laboratory tests, Monofrax® K-3 refractory was the most durable refractory in contact with molten glass containing halides and sulfates in concentrations consistent with HLW waste acceptance criteria.[3,4,18,22-25] In addition, Inconel® 690 is resistant to halide and sulfate attack in non-aqueous environments and could be used as the MOC for melter top-head components (dome heaters, etc.) and glass contact components.[3,4,18,26] However, the temperatures in the plenum space must remain high enough since if condensation occurs, Inconel® 690 is subject to pitting and crevice corrosion.[27]

Monofrax® K-3 refractory is an electrically fuse-cast solid solution of alumina-chrome with a complex chrome-alumina spinel. The composition of the refractory, as provided by the vendor, is given in Table 2-2. Additional compositional data regarding the REDOX of the Monofrax®K-3 were added by SRNL as given in Table 2-2. For Monofrax® K-3 refractory design, it is desirable to have all glass contacting surfaces known as the "hot face" of the refractory be as-cast instead of machined.[10,28] The surface against the mold has a denser, finer grain structure from cooling at a faster rate, and this results in higher resistance to corrosion.[10,28] The fusion casting of the large Monofrax® K-3 refractory blocks eliminates small cracks provoked by thermal stresses by requiring a longer and more gradual cooling cycle for the large block pours.[10,28] For the lining in the melt pool, it is better to use larger blocks and have fewer joints to grind and fit.[10,28] Generally, cracks normal or parallel to the inside face will not fail in service since the compressive forces in a geometrically round (cylindrical) melter will hold the block(s) together.[10]

Table 2-2. Monofrax® K-3 Composition as Provided by the Vendor and as Partially Analyzed by SRNL

Component	Carborundum Analysis (Wt%)[5]	Component	SRNL Partial Analysis[29]
Al_2O_3	58.6	Al_2O_3	--
Cr_2O_3	27.1	Cr_2O_3	--
MgO	6.1	MgO	--
SiO_2	1.6	SiO_2	--
Fe_2O_3	5.9	Fe_2O_3	0.4-0.5 wt%
FeO	reported as Fe_2O_3	FeO	5.4-5.5 wt%
Na_2O	0.3	Na_2O	--
Other	0.4	Other	--
TiO_2	not given	TiO_2	~0.5 wt% by XRD
ZrO_2	not given	ZrO_2	trace by SEM

Inconel® 690 is a high temperature, corrosion resistant specialty alloy. It has a minimum of 58 wt % nickel and a chrome range of 27-31 wt % (Table 2-3). It melts at approximately 1345 °C, so it is important to maintain melter operating temperatures below 1170 °C to avoid thermal creep of the metal.[8,12,13,30] In addition, above 1150 °C, the Inconel® 690 is susceptible to pure oxidation attack.[30] With adequate temperature control, Inconel® 690 maintains sufficient creep resistance for the massive self-supporting melter electrode components.[26,30] The high chromium content of the alloy (minimum specified for DWPF is 29 wt %, with 32 wt % as the ideal[12]) gives it exceptional resistance to oxidation and sulfidation. In other tests, Inconel® 690 resisted attack by sulfidation/oxidation agents, where a nickel based alloy with lower chromium content, Inconel® 601, was penetrated by these agents.[26,30] Inconel® 690 is protected at high temperatures by a layer of $Ni(Cr,Fe)_2O_4$ and $(Cr,Fe)_2O_3$ that forms during the initial heating period.[26] Inconel® 690 is very resistant to attack in non-aqueous environments; however, it pits in aqueous halide solutions if there is insufficient oxidizing acid present.[26]

Table 2-3. Inconel® 690 Composition[8]

Component	wt %	Component	wt %
Ni	58	Si	0.05 maximum
Cr	27 – 31	Mn	0.50
Fe	7 – 11	S	0.15
C	0.05 maximum	Cu	0.50

2.3 Melter Off-Gas System

The principal requirement of the DWPF off-gas system is removal of particulate contaminants from melter off-gases before they are exhausted to the atmosphere.[20] Additional requirements of the MOG system are removal of elemental (non-radioactive) mercury, maintenance of a controlled negative pressure in the melter in the presence of surges in off-gas generation rate, and dilution of hydrogen and carbon monoxide generated in the melting process to below the lower explosive limit.[20] The design of the DWPF MOG system began in the late 1970's and early 1980's. The configuration of the MOG system was centered on a patented hydro-sonic® scrubber (HSS) from Lone Star Steel Company.[31,32] The primary challenge in designing the MOG system was selecting a wet scrubber that was highly efficient in removing submicron size particles, more so than the off-gas quencher scrubber.[31,32] The HSS was modified to the needs of the DWPF and is now known as the steam atomized scrubber (SAS). The rest of the off-gas system was built to prepare the off-gas stream for the SAS and to handle the products from the SAS.

The DWPF Melter off-gas system is shown in Appendix A. To ensure the contaminated off-gases from the melter are always being removed and treated, the off-gas system has a backup (BU) off-gas system to ensure constant operation even during maintenance or idling periods.[33] The components of the off-gas system, MOC, and function are shown in Table 2-4. As originally designed, a film cooler brush was installed to keep the off-gas piping to the Off-gas Film Cooler (OGFC) clear of entrained deposits from the melt pool splatter.[33] However, it is not included in Table 2-4 as it was designed to be used on an as-required basis and to date, has not been installed in the MOG system after the non-radioactive operations during DWPF Melter #1 startup.[34]

Table 2-4. Off-gas system components, materials of construction and function.

Component	MOC	Function
Off-gas Film Cooler (OGFC)	Inconel® 690	Air addition, cool off-gas to 400 °C[35]
Primary off-gas line	Inconel® 690 (to isolation valve) Hastelloy® C-276 (to quencher)	Transfer off-gas, addition of dilution air
Quencher	Hastelloy® C-276 (Primary) Allvac® Allcorr® (BU)	Inject water into gas stream, cool gas to <60 °C
Off-gas Condensate Tank (OGCT)	Hastelloy® C-276	Collects condensate from the quencher, SAS, OGC, and HEME. Recirculates water back to the quencher.[33,35]
Off-gas Condenser (OGC)	Hastelloy® C-276	Condense vapors
Steam Atomized Scrubber (SAS)	Hastelloy® C-276	Removes small (< 1μm) particles, atomized condensate mixed with off-gas and water coated particles sent back to OGCT.[33,35]
High Efficiency Mist Eliminator (HEME)	Hastelloy® C-276	Glass fiber filters remove fine mists and particles in off-gas exiting the OGC.[20,33]
Preheater	Type 304L SS	Heats off-gas to ensure water does not condense in HEPA.
High Efficiency Particulate Air (HEPA) Filter	Type 304L SS	Two stage filter removes any remaining particulates.
Off-gas Exhauster	Type 304L SS	Draws off-gas vapors from the melter through the off-gas system components, maintains negative pressure on melter and MOG system.
Air tunnel/sand filter/stack	Type 304L SS	Final path for off-gas.

Hastelloy® C-276 is a nickel-molybdenum-chromium wrought alloy that is generally considered a versatile corrosion-resistant alloy.[36] C-276 alloy has excellent resistance to localized corrosion and to both oxidizing and reducing media. It has a minimum nickel concentration of 57 wt %, approximately 16 wt % chromium, 16 wt % molybdenum, and maximum carbon concentration of 0.01 wt % (Table 2-5).[36] Allcorr® (UNS N06110) is a high performance nickel-based alloy designed for service in highly corrosive atmospheres.[37] Du Pont evaluated the alloy for crucial off-gas service involving severe temperature and chemical exposures based on experience using Allcorr® in oil field down-hole applications.[37] The alloy consists of approximately 31 wt % chromium, 10 wt % molybdenum, and 56 wt % nickel (Table 2-5).[37,38] Type 304L SS is a variation on the basic Type 302 steel with a higher chromium and lower carbon content.[39] Lower carbon minimizes chromium carbide precipitation in welding and its susceptibility to inter-granular corrosion as well as corrosion resistance to a wide range of atmospheric, chemical and industry exposures.[39] Type 304L is an extra low-carbon variation of Type 304 with a 0.03% maximum carbon content (Table 2-5).[39]

Table 2-5. Composition of alloys used in DWPF off-gas system.

Component	Hastelloy® C-276[36]	Allvac® Allcorr®[37,38]	Type 304L SS[39]
	wt %	wt %	wt %
C	0.01 maximum	~ 0.020 – 0.030	0.08 maximum
Mn	1 maximum	0.01	2.00 maximum
S	--	~ 0.002	0.030 maximum
Si	0.08 maximum	0.02	0.75 maximum
Cr	16	31	18.00 – 20.00
Ni	57 (balance)	56 (balance)	8.00 – 12.00
Mo	16	10	--
Nb	--	0.40	--
W	4	~ 2.00	--
V	0.35 maximum	~ 0.02	--
Ti	--	0.25	--
Fe	5	~ 0.12	balance

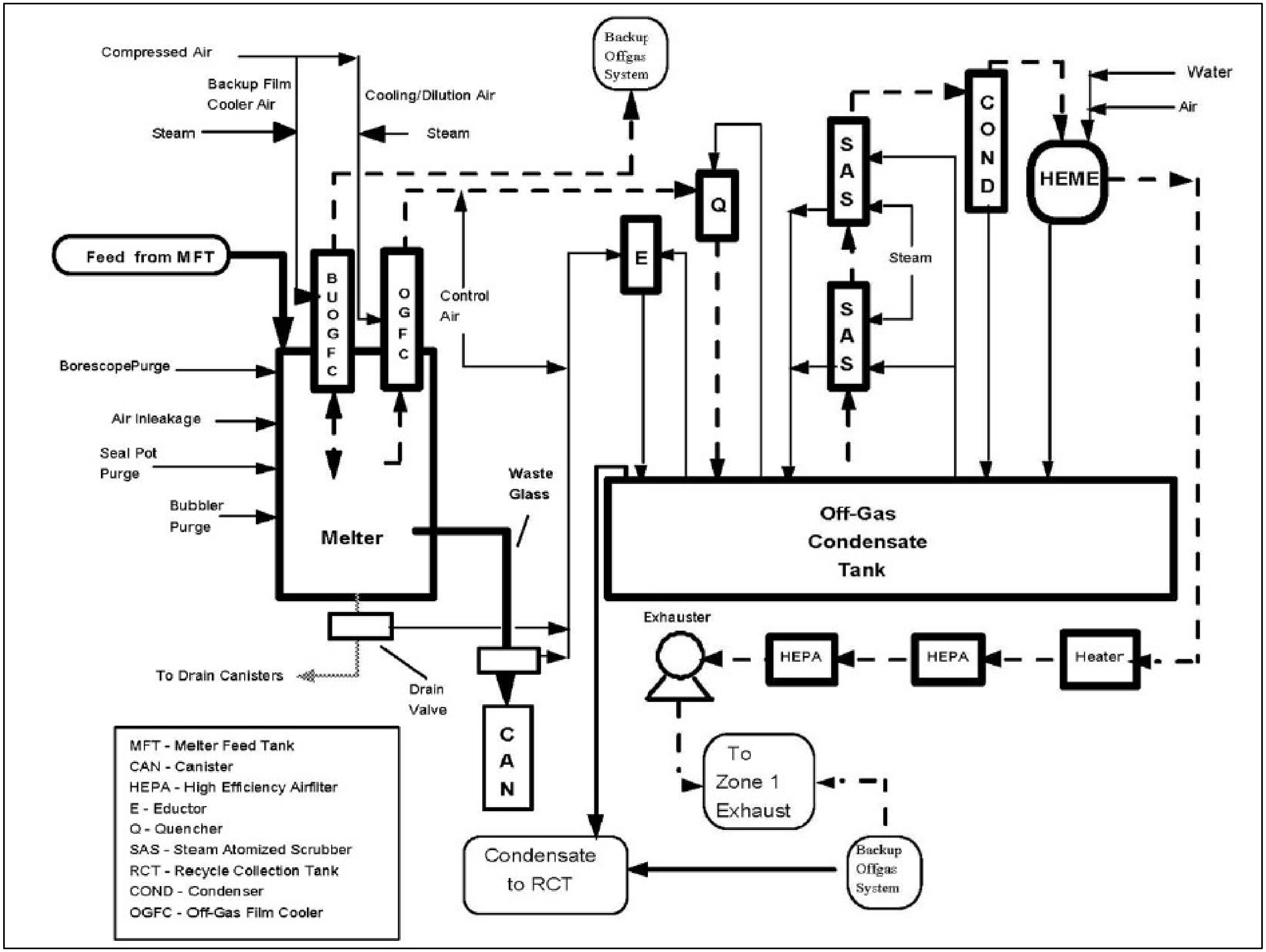

Figure 2-4. Schematic of DWPF off-gas system.

3.0 Coupon and Preliminary Testing

3.1 Refractory and Melter Top Head Components

Multiple coupon tests were performed in support of the DWPF Melter design.[3-5] The first tests, performed by Wicks in 1978 using simulant waste glass and a modified ASTM C621 test "Static Corrosion of Refractories by Molten Glass," showed that Monofrax® K-3 and Inconel® 690 both performed the best under static and dynamic conditions, with a reported erosion of 0.002 square cm for both MOC.[3] Subsequent tests using radioactive glass showed no abnormal corrosion, although the actual waste glass was slightly more corrosive than the simulated waste glass.[4] Wicks also performed a one year test, immersing both MOC in simulant waste glass held at 1050 °C, which is at the lower operating temperature of the DWPF Melter.[4] The corrosion after one year of immersion was 0.8 mils for Monofrax® K-3 and 0.11 mils for Inconel® 690.[4] Based on these data, it was concluded the ceramic-lined melters should easily meet the two year minimum design lifetime and could last up to 6 years in a canyon operation.[4] It should be noted that throughout the coupon testing, precipitation products[3,4] were observed on both MOC, which correspond to observations in the pilot scale melters[3,4,8,10,40] and analysis of the DWPF glass in Melter #1.[11]

Other coupon tests, all in pre-reacted glass, were performed to determine the effect of temperature, as well as frit and waste composition, specifically Na_2O, provided different corrosion rates, but did not refute that the melter would last more than two years.[22-25,41] These tests showed that refractory corrosion was increased by decreasing melt viscosity, increased alkali and SO_4 in the waste, and increased melt temperature.[22-25,41] One report showed that Inconel® 690 is approximately 2 – 6 times more corrosion resistant than the Monofrax® K-3 at 1150 °C under static conditions, which is the nominal operating temperature of the DWPF Melter.[10,23] Testing also showed that increasing the Na_2O concentration (3 -20 wt %) in the glass melt greatly accelerates the rate of penetration of both Inconel® 690 (2.5 X) and Monofrax® K-3 (1.3 X).[24] Similar effects are expected from increasing the concentration of any alkali in the glass.[24]

A review of melter lifetime by SRR in 2011 indicated that the refractory thickness of 12 inches was based on initial testing of the Monofrax® K-3 refractory resulting in a corrosion rate of 5.4 mils per day for the melter sidewall surface.[13] This rate translated into a loss of about 4 inches over the two year design life.[13] Subsequent testing indicated that the corrosion rates were about five times less; however, the design wall thickness for DWPF Melter Monofrax® K-3 refractory was not reduced from 12 inches.[13]

In 2003, there was concern about the chemistry of sludge batch 3 (SB3), specifically the increase in the sulfur concentration of the feed and the associated change in the glass solubility limit of this constituent (up to 0.60 wt %).[42] Sulfidation of nickel based alloys can occur in an oxidizing environment and the synergistic effect of impurities such as chlorine and sodium can further accelerate the degradation of the Inconel components.[42] Static molten glass corrosion tests were performed using simulant glass for up to 6 weeks at 1150 °C.[42] The glass was refreshed on a regular basis to account for the volatile compounds, including chlorides. Results showed that there is a detrimental synergistic effect of sulfate and chloride on the stability of the protective oxide layer which decreases the corrosion resistance of the Inconel® 690 in the molten glass and the vapor space; however, the corrosion rate was comparable to the established DWPF corrosion rate and therefore was not a concern.[42] It was concluded that over the lifetime of the melter, top head components will experience a higher corrosion rate than the glass contact materials as a result of sulfate and chloride deposition at approximately 550 °C.[42] As long as the temperature of the top head components is not in the range of 400 °C – 900 °C, the lifetime of the components should not be affected.

3.2 Melter Off-Gas Components

During scaled melter tests, Du-Pont conducted a rigorous down select of materials for the various MOG components.[43,44] For the purposes of material selection, the melter system was divided into high and low temperature regions.[30] Alloy selection began by summarizing waste types to be processed and definition of maximum anticipated concentrations of chemical species.[27] Computerized chemical process evaluation programs were used to determine recycle and processing effects on concentrations. The levels of 135 chemical species in 177 process streams were computed. Test solutions were formulated based upon major chemical components, acidic species, and ionized transition metals that are known to enhance general or localized attack (e.g. cupric and ferric ions).[27]

Alloy 20 (i.e. Carpenter 2OCb-3) was selected as the reference material for all process vessels operating below 300 °C in the melter feed preparation and melter off-gas areas.[27] This selection was primarily based on this alloy being the least expensive and most readily available alloy with virtual immunity to chloride stress corrosion cracking; however, additional materials were selected for testing which offered superior corrosion resistance relative to Alloy 20.[27] A primary reason to carry backup or alternative materials forward in the testing program was the concern that the relatively high copper content of Alloy 20 (3.5 %) might cause accelerated attack by the high mercury content of the radioactive waste.[27] Inconel® 690 was selected as the reference melter alloy based upon demonstrated oxidation and sulfidation resistance in engineering melter tests.[26,45] However, the greatest uncertainties remaining after preliminary evaluation involved the interactions between formic acid, halides, mercury and abrasion in the feed preparation areas and corrosion effects of mercury in the MOG.[27] The presence of mercuric chloride, low pH, and elevated temperatures, makes the MOG condensate the most corrosive stream in the DWPF.[30] In order to address these concerns, a small scale melter test was contracted to Pacific Northwest Laboratory (PNL) to expose metal coupons to mercury, and higher halide concentrations than possible in engineering scale equipment.[27] Tests were run for 1 to 2 weeks at higher-than-anticipated concentrations, under submerged, vapor space and condensate conditions.[27] In addition, two-liter flasks with attached condensers[46] were run under total reflux conditions and parameters evaluated included alloy composition, temperature, pH, halide concentration, crevices, stresses, welds, and form of mercury.[27]

Further off-gas corrosion tests were based upon results of the laboratory melter tests, specifically the chemistry processed by the quencher solution (pH is 2.2, or higher, with a major fraction of the mercury as mercuric chloride).[27] Examination of the melter after testing revealed that Inconel® 690 is not locally attacked where temperatures remain above the condensation point of the salts. However, severe pitting was seen after one month's operation of the Inconel® 690 off-gas quencher; therefore, the quencher became an area of special study.[27] It should be noted that the melter's Monofrax® K-3 refractory experienced no unusual attack, confirming that Inconel® 690, and Monofrax® K-3 refractory are suitable for melter construction.[27] Based upon this test, Inconel® 690 was retained as the melter reference material. Metal samples exposed in the melter OGCT indicated that highly alloyed nickel-based alloys are required to restrict crevice corrosion and pitting.[27] In fact, testing showed that all alloys with a total chromium plus molybdenum content exceeding 30 wt% were able to resist crevice corrosion in simulated process solution at pH 6 and 40 °C.[27] Only nickel based alloys with a minimum of 9 wt% molybdenum were able to resist crevice attack at pH 1.6 and 40 °C, and only Hastelloy® C-276 and Allcorr® resisted localized attack at pH 6 and 90 °C.[27] Allcorr® was the only alloy tested that could resist pitting and crevice corrosion at pH 1.6 and 90 °C.[27]

Additional alloys were investigated during laboratory testing to approximate off-gas quencher conditions and, of the alloys tested, Hastelloy® C-276 was the only alloy with a high resistance to both general and localized attack.[27] Localized attack was especially severe in Alloy 20 exposed to melter off-gas condensate, and directional pitting produced holes completely through 1/4 inch samples in 72 hours.[27,43,44] Since Alloy 20 performed so poorly in coupon tests, it was removed as the reference material for melter feed preparation and MOG systems, and Hastelloy® C-276 was selected as the new reference material for these process zones.[27,43,44]

After scouting tests had determined the relative ranking[43,44] of alloys under nominal conditions, it was necessary to verify the material selection using prolonged exposure times, realistic process cycles, and equipment with construction methods and details similar to actual vessels.[27] Extended tests were performed in Demo flasks[46] to simulate the extremes of pH and temperature for times equivalent to one year of operation resulting in negligible corrosion of Hastelloy® C-276. At the conclusion of these tests, Hastelloy® C-276 was selected as the material of choice for the low temperature region (< 60 °C) and Allvac® Allcorr® was selected for the quencher because of the slightly better performance than the Hastelloy® C-276 at higher temperatures (however C-276 was also considered to be satisfactory for the quencher).[27,30,43,44] Additional testing by SRNL concluded that the components in the dry, unwetted, high temperature region (melter electrodes, piping from the melter to quencher) should be fabricated from Inconel® 690.[27,30] If condensation occurs, then Inconel® 690 is subject to pitting and crevice corrosion.[27] Testing also determined that Type 304L SS is satisfactory for general service piping and tankage in the DWPF; however the combined effects of elevated temperatures, re-acidification, and concentration of corrosive agents make Type 304L unacceptable for use with process solutions derived from sludge.[27]

4.0 Scaled Melter Testing

The SRNL has operated five pilot-scale melters in support of the design of the DWPF since 1976 in order to verify or improve the DWPF Melter and off-gas system design.[10,11] Typically, the scale of these melters was based on the melt pool surface area and therefore melting rate achieved in relation to the DWPF Melter design basis.[11] Table 4-1 shows average measured wear rates for the Monofrax® K-3 and Inconel® 690 for each pilot scale melter. These five melters were all operated with natural convection and all were of a geometrically circular design, except for the Large Slurry Fed Melter (LSFM) which had a square design. A compiled list of the melt history and glass compositions processed in various SRS pilot scale melters can be found in reference [10]. The majority of the melters were run with a reducing flowsheet, similar to the DWPF flowsheet, but some pilot scale melters ran oxidizing or calcine flowsheets (Table 4-1). As discussed in this section, the REDOX of the flowsheet impacts the wear rates of the melter MOC.

Table 4-1. SRS Pilot Scale Melters – Monofrax® K-3 and Inconel® 690 Wear Rates

Melter Designation	Average Refractory Wear Rate			Average Inconel® 690 Wear Rate	Flowsheet
	Above Melt Line	0 – 4" Below Melt Line	Throat / Riser	Electrodes/ Thermowells	
Project 1941	nm	nm	1 in/yr[47]	0.5 mils/day[47]	Dry Calcine
SCM	5.5 mils/day[48-50]	7.5 mils/day[48-50]	11 – 13 mils/day[48-50]	1.36 – 1.71 mils/day[48,50]	Dry Calcine & Reducing Slurry
LSFM	1 mil/day[26]	1 mil/day[26]	nm	0.3 mils/day[26]	Reducing Slurry
SGM	nm	nm	nm	nm	Reducing Slurry
IDMS	nm	nm	nm	~ 12 % material loss[8]	Reducing and Oxidizing Slurries
TDS Design Basis[51]	3 mils/day	7.5 mils/day	12 mils/day before Inconel® 690 lined	1.3-1.8 mils/day	Reducing Slurry

nm – not measured (based on the findings of this literature search)

4.1.1 Project 1941 Melter

The Project 1941 Melter was the first prototype melter system tested at SRS. The Project 1941 Melter was cylindrical and approximately one half of the DWPF melt pool surface area.[11] Appendix A shows the cross-section view of the Project 1941 Melter. The main differences between the Project 1941 Melter and the DWPF Melter result from the Project 1941 design basis:[10]

- The melter was initially fed with dry calcined oxide sludge. Slurry feeding was demonstrated later.
- No nozzle penetrations were permitted in the vessel below the glass melt surface except for the drain valve.
- Minimum design-life for the melter and its components was two years.
- Riser was lined with Monofrax® K-3 not Inconel® 690.

One of the major objectives of the Project 1941 Melter program was to characterize the corrosion rates of the materials in contact with molten glass.[47] The Monofrax® K-3 and Inconel® 690 alloy were chosen for the glass contacting refractory and electrodes, respectively, after visits to PNL and Penberthy Electromelt in 1976.[10] Later tests confirmed that Monofrax® K-3 had the best corrosion resistance of commercially available refractories.[10] Similar tests established that Inconel® 690 had the best corrosion resistance of commercially available metals.[10]

The Project 1941 Melter had a slanted riser design, similar to the riser in the current DWPF Melter design. The slanted riser differed from other experimental glass melter designs where the conventional riser is vertical or near vertical, followed by a horizontal trough leading to the pour point.[10] There are inherent drawbacks to the vertical or near vertical configuration:[10]

- The vertical construction allows glass to contact both sides of the refractory walls above the throat (entrance to the riser). This subjects the critical throat area to glass corrosion on the inner and outer walls, doubling the corrosion rate.
- Monofrax® K-3 refractory will corrode at an accelerated rate if it is in the path of electric current or in the flux field between electrodes. With a vertical riser, such as the one used in an early PNL experimental melter, the throat wall is in the direct path of any electric current passing from melt pool electrodes to the riser heater. Cracks and openings in the unconstrained throat blocks will increase the occurrence of electrical short circuits.

These considerations led to the DWPF slant riser design. Later, severe attack of Monofrax® K-3 throat blocks occurred on two experimental melters that had a vertical riser design.[10] These resulted from the combination of geometry and electrical effects noted above.[10] Additional details of the Project 1941 Melter design can be found in reference 10.

The Project 1941 Melter was built and run in campaigns from approximately 1978 to 1981 (Table 2-1). The melter was maintained at a glass temperature of approximately 1130 °C for 398 days during which it operated in both calcine-fed and slurry-fed mode.[47] However, during the first three months of operation, the melter temperature was inadvertently controlled at a temperature above 1200 °C, and for approximately seven days in that time period, the melter temperature was approximately 1300 °C.[52] The Project 1941 Melter experienced two periods when the temperature was below 1018 °C, the liquidus temperature for Frit 131 and Technical Data Summary (TDS) glass.[52] The first was between the dry calcine feeding campaigns and a crystalline layer approximately seven inches thick formed on the bottom of the melter after idling at 1050 °C for 58 days.[10,11,47] The second was when the melter was shut down periodically while converting between calcine-fed and slurry-fed operations.

Upon shutdown, the Project 1941 Melter was disassembled to evaluate materials performance and assess its service life.[52] During calcine feeding, a crystalline layer approximately seven inches thick formed on the bottom of the melter.[10,11,47] During the initial glass melting startup period, instrumentation problems resulted in variations in the glass melt temperature.[10,12] As a result, the bottom of the melter was below the liquidus temperature of the glass.[10,11,52] An additional one inch layer of crystalline deposits were observed on the melter walls as well as in the riser and nozzle. The deposits had almost completely plugged the riser from the crystalline material that had accumulated on the bottom of the melter to the extent that deposits were being flushed out of the melter with the waste glass.[52] Analysis of the deposits showed that some of the spinel accumulation could be attributed to corrosion of the refractory.[6,11,52] The Project 1941 Melter had a bottom temperature of 850 °C, which is below the liquidus temperature of the glass, while the bulk glass was 1150 °C. It was concluded that proper design and insulation of the melter bottom and control of operating conditions would have produced an acceptable glass, while minimizing spinel formation as well as refractory and Inconel® 690 corrosion.[10,12,13,47]

While the formation of spinel at the bottom of the Project 1941 Melter is largely attributed to melter temperature variations[47], corrosion of the refractory did contribute to some spinel formation.[11,52] The molten glass reacts with both the Cr rich and Al rich phases of the refractory.[52] The reaction with the Cr rich phase forms a $Ni(Fe,Cr)_2O_4$ spinel, while reaction with the Al rich phase produces a glass that is enriched with aluminum.[5,29,52] The $Ni(Fe,Cr)_2O_4$ spinel particles spall off the surface of the refractory and into the melt pool. Increasing the melt temperature not only increases the corrosion rate of the refractory, but also reduces the viscosity of the glass, making the spinel layer more susceptible to being removed from the bulk refractory and into the glass.[52] However, despite some corrosion, examination of the Monofrax® K-3 refractory after shutdown showed that it was in excellent condition and measurements of the refractory showed 600 mils of the Monofrax® K-3 were lost at the melt line.[10,47] The maximum measured corrosion rate was 1 inch per year, about one quarter of the design basis in the TDS, which occurred in the throat.[47]

Analysis of the Inconel® 690 components concluded the observed wear supported the two year design basis.[52] The electrodes and thermowells exhibited an average corrosion rate of 0.0005 inches per day and this rate agreed with earlier data if the idling and running periods are considered separately.[47] It was calculated that the corrosion rate for the Inconel® 690 components in the Project 1941 Melter (assuming the melter is maintained at 1150 °C) was 0.0005 inches per day.[47]

4.1.2 Small Cylindrical Melter (SCM)

The Small Cylindrical Melter (SCM) had a melt pool surface of 1.3 ft^2 and was designed to test the performance of the various materials of construction when subjected to a variety of simulated waste and frit compositions.[53] The SCM began operations in October 1979 and produced 24,511 pounds of glass in the first two campaigns which were dry powder feeds of simulated average (the basis for the TDS glass composition) sludge with either Frit 21B or Frit 211.[11] The third campaign began as dry fed TDS sludge and Frit 131 and produced 27,010 lbs of glass.[11] The second part of the third campaign was slurry fed using TDS sludge and Frit 131 and produced 11,359 lbs. of glass.[11] Further details of the glasses produced using the SCM can be found in reference 11.

During the first operating campaign, the melter was fed eight hours a day until an electrode failure caused the melter to be shut down and drained after approximately 4.5 months of operation. The second campaign lasted for 133 days when a failure at the refractory throat caused the SCM to shut down.[50] Evaluation of the MOC showed the most refractory wear was 2 – 3 inches below the melt line.[50] It should be noted that three times more glass was produced in Campaign 2 than Campaign 1 but the average maximum refractory wear rate only increased by 39%, indicating that the dominant factor of the wear rate of the melter sidewalls is glass temperature, not chemical attack tied to throughput rate or erosion.[50] The maximum average refractory wear was measured to be approximately 5.53 mils/day on the sidewalls and 11 – 13 mils/day at the throat, similar to the TDS value in Table 4-1.[48,49,54]

The riser in the SCM was lined with Monofrax® K-3 refractory and showed accelerated wear. It should also be noted that after approximately 10 months of operating the SCM, a hole was observed in the four inch thick Monofrax® K-3 refractory throat block near the top of the riser.[54] During SCM Campaign 1[48] and Campaign 2[50], it was hypothesized that the Monofrax® K-3 refractory lining the riser was dissolving associated with the high molten glass velocities, indicating that erosion could be degrading the refractory.[49] To address this finding, an idea was proposed to make the entire throat, riser, and pour lip section from Inconel® 690.[54] A large, flat, uncooled plate was installed at the base of the throat and the riser was lined with a thick walled piece of Inconel® 690, thick enough to provide a two year lifetime (corrosion based) as well as provide sufficient heat transfer area.[54] Lining the riser with Inconel® 690 is now the current DWPF design.

During Campaign 1, severe corrosion of the Inconel® 690 was observed in hot oxidizing environments and from sulfidization.[48] The Inconel® 690 electrode and thermowell wear rates were determined to be 1.36 – 1.71 mils/day (0.50 – 0.62 in/year).[48,54] The maximum wear rate on the Inconel® 690 electrodes occurred at approximately 4 – 5 inches below the melt line. Even with the increased volume of glass poured in Campaign 2, there was no measured increase in the electrode corrosion rate.[50] Based on the operation of the SCM, Monofrax® K-3 refractory wears approximately three times faster than Inconel® 690 in a reducing melt pool.[50]

4.1.3 Large Slurry Fed Melter (LSFM)

The Large Slurry Fed Melter (LSFM) was the second large scale melter tested at SRS for the DWPF program[10] and was a progressive step in reaching the final melter design or DWPF.[47] Primary objectives of this design were to evaluate slurry feed operations and off-gas components with various glass formulations.[47] It was also a test platform for several components, including a new electrode configuration, previously untested in pilot scale melters, but prototypic of the DWPF design.[10] The vessel was cylindrical with a flat floor and roof.[10] The throat and riser were made from Monofrax® K-3 refractory.[20] Several layers of backup refractory and insulation board were used, as the vessel was not water cooled. Glass was poured by tilting the vessel since differential pressure pouring was not feasible since there was a large amount of air in-leakage under vacuum.[10] Among the components tested in the LSFM, three were near prototypes of the DWPF configurations: electrodes, off-gas film cooler, and a thick wall thermowell.[10] A cross-sectional view of the LSFM melt chamber is shown in Appendix A.

The LSFM melter was run in campaigns over a period of 749 days.[10,26] During this time, the melter was operated with slurry feeding for 193 days (25%) and the rest of the time (75%) was spent idling at 1150 °C.[10,11] A total of 234 tons of glass were produced.[10,11] While the "L" shaped electrodes did demonstrate some ability to increase power to the bottom of the glass melt, it was not enough to achieve the desired control. This result led directly to the use of separate electrodes with independent power supplies on the DWPF Melter.[10]

The LSFM was also used to design and test the OGFC and other MOG system components.[19] During operation of the OGFC, it was reported that off-gas line pluggage problems were alleviated by cooling the off-gas to 350 °C – 450 °C and operation of the off-gas film cooler brush.[14,19,20] The ninth melter campaign of the LSFM successfully demonstrated extended operation of both melter and off-gas systems.[14] Two critical problem areas associated with the handling of melter off-gases were resolved leading to firm definition of the DWPF Off-Gas Treatment System.[14] These two concerns, wet scrubber decontamination efficiency, using the SAS, and the reduction of solids deposition at the off-gas line entrance, were the primary focus of off-gas system studies during the 63-day run (LSFM-9).[14] The HSS (now SAS) was confirmed to be the superior candidate for wet scrubbing by outperforming all other scrubbers tested.[14] The combination of the SAS and OGFC adequately resolved the deposit accumulation problem and both devices were incorporated in the DWPF design.[14] Throughout testing of the off-gas system components, the only concern noted was plugging, and there was no mention of corrosion of the components.

Maximum corrosion loss from the Monofrax® K-3 was less than 0.75 inches at the melt line and immediately above the throat, corresponding to a corrosion rate of approximately 1 mil/day.[26] Since the throat area had the most refractory wear, it was determined that the DWPF melter throat and riser should be lined with Inconel® 690 to reduce corrosion in that area.[20] An analysis of the Monofrax® K-3 refractory was made at the conclusion of the run by the Carborundum Company and it was concluded that the corrosion mechanism for K-3 is a function of the nickel and iron oxides in the glass.[10,26] Above the melt line, the refractory was in good shape, but some spalling occurred in the blocks located closest to the slurry feed tube.[10,26] This was assumed to be thermal shock fracturing caused by slurry feed water contacting the hot refractory but this does not occur in the DWPF Melter for the following two reasons:[10]

- The DWPF Melter feed tube is 20 inches from the refractory wall vs. 8 to 12 inches in the LSFM melter. For comparison, the centrally located feed tube in the Project 1941 Melter and SGM was 24 inches from the wall. Note that in September 2010, bubblers were installed in Melter #2, changing the configuration of the top head components as described in section 2.1.
- Based on the LSFM experience, Carborundum suggested lining the melter sidewalls with layers of Fiberfrax® paper between the Monofrax® K-3 and the melter shell. This acts as a sacrificial thermal barrier to protect the refractory from thermal shock during slurry feed start-up. This technique was used for the SGM start-up, and is part of the DWPF Melter component installation procedure.

There were no riser or pour spout pluggages reported during operation of the LSFM and approximately 0.5 inches of crystalline deposits were observed on the bottom of the LSFM when it was bottom drained.[26]

The Inconel® 690 parts in the LSFM were in excellent condition upon autopsy.[26] The corners of the electrodes showed general rounding and little material loss. The largest decrease in electrode thickness was 0.23 inches or 0.3 mils/day adjacent to the top edge of the footed ("L" shaped) electrodes, indicating several more years of service life was available.[26] Other Inconel components showed similar or less wear; however, the highest rate of attack was on the replaceable liquid level detector at the melt line (approximately 3.5 mil/day).[26] This bubbler type detector functions by determining the hydrostatic head difference between a vent above the glass melt and argon bubbled into the glass pool at a fixed location above the melter bottom.[26] During 492 days of continuous service, with an argon flow rate of 3 standard cubic feet per hour (scfh), the discharge hole was vertically enlarged at an average rate of 3.5 mils/day from high local glass velocities as bubbles rose from the vent.[26]

4.1.4 Scale Glass Melter (SGM)

In mid-1982, it was apparent that the configurations of many DWPF Melter components would differ from those tested in the Project 1941 and LSFM melters.[10] As part of the general plan to verify new designs through tests of full scale and prototype configurations, Project S-4234 was approved to convert the Project 1941 Melter vessel to the DWPF configuration.[10] The primary objective of the scale melter program was to verify operation of DWPF Melter equipment designs, including the following:[10]

- melter components: electrodes, dome heaters, riser/pour spout heater, pour spout bellows, thermowell, feed tube, level dip tube, and TV. camera/borescope
- bottom refractory and insulation design

- vacuum pouring (full scale DWPF canisters were poured)
- recirculating loop slurry feed system
- off-gas system equipment

The Project 1941 Melter had a 4 foot melt pool diameter, a 2/3 geometric scale of the 6 foot DWPF design. This same 2/3 ratio was applied to the electrodes and melt pool depth to simulate the DWPF glass melting process and control of glass temperature in the SGM. Scaling was not applied to the external dimensions of the dome heaters, riser/pour spout heater, and thermowells, since it was desirable to test electrical heating assemblies at the full size cross section. A cross-sectional view of the SGM is shown in Appendix A and additional details of the SGM design can be found in Reference 10.

The SGM produced approximately 90 tons of glass in two years using a reducing flowsheet and Frits 165, 168, and 200.[11] Additional details of the campaigns run with the SGM and the associated glass can be found in Reference 11. When the SGM was probed and drained after Campaigns 5 and 9, respectively, no significant accumulations of deposits were observed.[55,56] The lack of crystal formation in the LSFM and in the SGM melters has been attributed to better melter design, slurry feeding rather than pre-calcining (dry feeding), control of rheology, REDOX control using refluxed formic acid addition, and more solubilizing frit compositions.[11,26,55,56]

An unexpected problem was observed on the SGM following Campaign 8, when a thermowell was removed after 20 months of continuous service. The tube had a pronounced J shape in the immersed section, which was attributed to glass convection currents exerting enough force to deform the Inconel® 690 tube at 1150 °C.[10] Thermowells were intended to be replaced every two years in the DWPF, but researchers recommended reducing this time to one year based on the SGM experience.[10] It was thought that even one year may be too long, since a slight bend at the bottom may make the vertical extraction through a melter port difficult,[10] and the thermowells were never removed from the SGM. It should be noted that although the design life of both the melt pool thermowell and level probe were considered to be less than two years, there has never been such a failure in either Melter 1 or 2[12] and the thermowells have not been removed from either melter; however the level probe had to be replaced once in Melter #1 due to erosion/corrosion.[57]

The SGM exhibited problems with off-gas line pluggages between the OGFC and the quencher; however, the pluggages were at greater distances from the off-gas line entrance than the pluggages in the SCM and LSFM.[19] Analysis showed the deposits plugging the MOG system in the SGM were from operational control of the system[19] and there was no reported evidence of corrosion in the MOG components.

4.1.5 Integrated DWPF Melter System (IDMS)

The Integrated DWPF Melter System (IDMS) was designed and constructed to provide an engineering-scale representation of the DWPF Melter and its associated feed preparation and off-gas treatment systems.[58] The IDMS was similar to the SGM but the Monofrax® K-3 refractory lining was made thicker to achieve a smaller, two foot diameter melt pool.[13] A cross-sectional view of the IDMS is shown in Appendix A. The IDMS was primarily run to investigate DWPF feed preparation (melting rate of simulants, etc.) and materials of construction issues.[13] A secondary objective was to determine the impact of noble metals in the melter.[13] The IDMS MOG system was a scaled simulation of the DWPF system and had all the DWPF off-gas components, except for the backup off-gas system.[58]

Selection of the materials for use in the DWPF required numerous materials to be evaluated at the laboratory scale (section 3.0) and the culmination of these tests was the IDMS materials evaluation program.[16] During this program, sample coupons of 26 different alloys were subjected to process conditions and environments characteristic of the DWPF except for radioactivity.[16] As part of this program, fifteen corrosion racks were assembled and placed in various vessels and process piping in the feed preparation, melter, and off-gas system and locations where corrosion/erosion related problems were anticipated.[16,17] This materials program also included visual characterization and inspection of the melter MOC during and after operation of the IDMS. The results of the program are described in the following sections.

During seven years of continuous operation (30% feeding, 70% idling), the IDMS poured approximately 46,400 pounds of glass based on Frits 165 and 202 with a reducing flowsheet, approximately 45,200 pounds of glass based on Frit 202 (28 tons total processed with a reducing flowsheet), and approximately eight tons (16,000 pounds) of oxidizing nitric acid flowsheets.[8,11] During this time, the off-gas system was always operating. Based on melter feed noble metals analyses, a total of 26.l pounds of ruthenium, 5.l pounds of rhodium, 9.0 pounds of palladium, and 3.4 pounds of silver were fed to the IDMS Melter during thirteen slurry-fed runs. The analysis of the melter MOC indicated noble metal accumulation could affect refractory corrosion.[8,13] Two runs without noble metals occurred during this time frame as well. Per analyses of samples of glass poured into each canister, the main noble metals that remained in the melter were ruthenium (9.2 pounds or 35% left in melter) and rhodium (1.1 pounds or 22% left in melter).[8,13] Analysis of core drilled samples of the glass deposits in the bottom of the melter showed that the glass contained 0.016 – 0.026 wt% palladium, 0.022 – 0.041 wt% ruthenium and 0.007 – 0.012 wt% rhodium.[8] The deposition of noble metals was observed to be greater when the melter was idling, not feeding and pouring, which was about 70% of the operation of IDMS. The reason for this is believed to be that the noble metals were flushed out of the IDMS Melter when pouring was being performed.[8,12,13,59] The melt pool was not agitated other than by normal convection currents.

After completion of the IDMS testing program, the melter was shut-down, de-inventoried and inspected to perform a melter autopsy.[8,12] The IDMS had accumulated 12 inches of glassy and crystalline deposits on the melter bottom; however, the bottom drain valve failed so the melter was drained via the pour spout by suction. A portion of the deposits, therefore, resulted from glass that could not be drained from the melter.[8,11]

4.1.5.1 IDMS Melter MOC

The Monofrax® K-3 refractory had some thinning and spalling at the melt line.[8] Several pieces of refractory were missing near the upper electrode, and there was aggressive attack of the K-3 near the drain region in the bottom of the melter.[8] As much as 2 inches of K-3 was missing near the drain valve and a canal had been worn on one side of the melter floor between one lower electrode and the drain valve.[8]

The Inconel® 690 dome heaters were in excellent condition.[8] The top of the upper electrodes above the melt line were in good shape, but the bottom of the upper electrode showed some wear (loss of material and rounding of edges).[8] The lower electrodes experienced more wear, as they had lost about 12% from their faces.[8] The Inconel® 690 riser and pour spout were in good condition, although there was corrosion noted in the unheated lower portion of the pour spout.[8]

Core samples of the glass showed that the composition was consistent among the samples and that no enrichment of any oxide species versus the nominal glass compositions tested was apparent.[8] Analysis of deposits from the melter floor had a high concentration of Cr_2O_3, Fe_2O_3, and ZrO_2, with a slightly high concentration in Al_2O_3 and MgO. It is believed that some of the enrichments (Cr_2O_3, Fe_2O_3, and Al_2O_3) resulted from the degradation of the Monofrax® K-3 refractory, while others (ZrO_2) were attributed to the various waste feeds run through the IDMS.[8] It is unclear from the chemical analysis of the deposits if the K-3 attack occurred over the seven year lifetime of the IDMS, or the attack occurred preferentially during feeding of the oxidized nitric acid flowsheets.[8] These lower deposits contained 27-66 wt % spinel and up to 9 wt % noble metals. Many of the problems observed, including the wear of the lower electrodes and channeling at the melter floor from the drain valve to a lower electrode, can be attributed to the deposits of conductive noble metals.[8]

4.1.5.2 IDMS Off-Gas System MOC

On January 17, 1992, after four years of IDMS operations, the corrosion coupons were examined as part of the materials evaluation program.[60] This was an interim visual inspection and overall, no significant corrosion was observed on any of the coupons and they were replaced in the IDMS a few days later.[60]

In April, 1993, all the corrosion racks, except from the melter and melter stack, were removed for examination.[61] When the coupons were removed from the off-gas system, they were inspected for crevice corrosion, pitting, stress corrosion cracking, general corrosion, and abrasive wear.[16,60,61] All the coupons in the quencher inlet region exhibited localized corrosion. Allvac® Allcorr® and Inconel® 690, which are used in DWPF MOG system, showed significant corrosive attack, but not sufficient to affect the operating life of the component.[16,61] Alloy C-22 and Alloy 625 coupons also exhibited superior corrosion resistance in the quencher.[16,61] Pitting was observed in the Type 304L SS coupons in the OGC inlet and the HEME inlet downstream of the quencher.[16,61] It should be noted that the IDMS OGC and HEME were fabricated from Type 304L and corrosion is not expected in these DWPF components since they are fabricated from Hastelloy® C-276.[16,61]

On August 8, 1995, after the IDMS was shut down, remote visual inspection of the IDMS off-gas quencher, SAS inlet, HEME outlet, HEPA inlet and associated piping did not reveal any evidence of significant corrosion attack.[15]

5.0 DWPF Melter

5.1 DWPF Melter #1

The first DWPF Melter began non-radioactive operations in April 1994 with oxidizing flowsheet simulated feeds. Radioactive operations began in 1996 and were also initially based on an oxidizing flowsheet. Approximately 2,713.5 tons (5.43 E05 pounds) of HLW radioactive glass were processed through Melter #1, which is equivalent to over 1300 canisters and five million curies of radioactive material.[5,12] In order to better ensure the reliability of DWPF remote canyon process equipment, a materials evaluation program was performed as part of the overall non-radioactive startup test program.[62] The test programs included erosion/corrosion studies of the process vessels for melter feed preparation and inspection of the melter and off-gas system.[30,62] Corrosion coupon racks were installed in the OGCT and select melter feed preparation vessels in both the liquid and vapor regions.[30]

In 1995, after non-radioactive operations were complete, the melter off-gas and top head components were visually inspected to ensure they could meet the two year design life.[34,40,62] No significant degradation was observed except for oxidation of the borescope[63] degradation of the film cooler brush, and minor oxidation on the film cooler.[21] The borescope outer housing showed significant degradation[63], but the lifetime was extended by changing the alloy to Inconel® 693 (Cr/Ni/Al); however applying a Cr/Al duplex coating was also considered.[34,40] As a result of the initial degradation, these borescopes were never used by DWPF again.[57] The feed tubes also showed significant degradation (end grain attack) but their lifetime was extended by a weld overlay.[34,40] The primary film cooler brush was fabricated from Hastelloy® X (alloy containing 9 wt % molybdenum) and showed severe degradation from oxidation of the molybdenum in the brush bristles and the resulting MoO_3, a corrosive gas, contributed to pitting of the brush block and further degradation of the bristles.[34] The backup film cooler brush performed satisfactorily during non-radioactive runs; however similar degradation is expected if the backup system is used continuously.[34] It was proposed that the MOC for the film cooler brush bristles be changed to

Inconel® 690 with other alloy modifications to prevent oxidation since Hastelloy® X does not perform satisfactorily in the DWPF environment;[34] however the film cooler brush was never re-installed in the MOG. Other components were visually inspected but determined that they could meet the two year design life.[34,40]

A decision was made to eliminate the planned inspections of the DWPF off-gas system downstream of the quencher based on prior inspections of the IDMS.[15-17,60-62] As discussed in section 4.1.5, field inspections and review of the corrosion coupons removed from the IDMS off-gas system, as well as maintaining sufficient velocity in the off-gas line, demonstrated that corrosion in these components was not a concern.[15-17,60-62] Inspection of the MOG line from the film cooler to the isolation valve showed severe pitting just below the film cooler brush flange and the metal surface was covered with a light grey deposit.[64] It was expected that the MOG line at the melter (Inconel® 690) would require replacement from pitting corrosion after three years[62]; however, there are no records of the MOG line being replaced or failing from localized corrosion at the time of this report. The primary quencher was the only off-gas component fabricated from Allvac® Allcorr®.[64] Although there were some deposits on the quencher, there was no evidence of corrosive attack.[64] Investigation of the BU off-gas system, which is the same as the primary except the quencher is fabricated from Hastelloy® C-276, showed some deposits throughout the system, but there was no evidence of corrosion except for the film cooler brush.[64] Based on the inspections of the MOG system after non-radioactive startup runs and the performance of the components during the IDMS campaigns, the SAS, HEME, and OGCT vessels predicted service lives were expected to meet or exceed their 2 – 5 year design life.[16,34,61,62]

Glass pouring problems were experienced by the DWPF Melter during cold runs prior to radioactive operations.[12] The degradation of the Inconel® 690 pour spout knife edge at the glass disengagement point was a main source of the problem.[12] A replaceable insert for the pour spout, which re-establishes the corroding knife edge, was installed in the DWPF Melter and pour problems were greatly reduced and canister production rate was doubled.[12] Discussion of other modifications to increase melter life, other component failures and melter process operational requirements are discussed in Reference 10.

In March 1996, radioactive operations began.[13] In May 2000, the center thermowell was removed and visually inspected, showing only melt line attack and was in otherwise good condition.[21] In April 2002, the dip tube bubbler melt level detection device was removed because of through wall attack on one side of the tube at almost 30 inches below the melt line.[21] Also in 2002, Melter #1 had lost one set of vapor space (dome) heaters and was experiencing ongoing glass pour stream instabilities, which had negatively impacted the DWPF glass production rate. Resulting from the combination of an extended DWPF outage and the failure of a dome heater, Melter #1was shut down for replacement in November 2002.[13]

The bottom of the melter (lower electrodes and below) was not inspected because the glass was not completely drained from the melter because of the failure of the drain valve; therefore, it is impossible to comment on the condition of the lower electrodes and lower parts of the refractory. Analysis of Melter #1 post-shutdown showed that the K-3 refractory was in excellent condition with minimal spalling at the melt line.[13] Based on the inspection of Melter #1, the refractory corrosion rate was determined to be much lower than the value used to set the two year design life basis.[12,13,21] Based on the performance of Melter #1 and the desire to increase melting rate and therefore throughput, Savannah River Remediation (SRR) proposed reducing the refractory wall thickness from 12 inches to 10 inches in 2007.[12] Reducing the refractory wall thickness would increase the melt pool surface area leading to greater throughput. However, after this 2007 study, bubblers were installed in the melter in September 2010, which have resulted in melting rates above 200 lb/hr such that a reduction of the K-3 refractory thickness was not warranted.[12,65]

Only the upper electrodes were visible for end of life inspection in Melter #1. The corners and edges showed rounding below the melt line and the electrodes were deflected downward.[12,13,21] Further inspection showed this deflection was likely thermal creep from Melter #1 operating up to 50 °C higher than the 1150 °C design temperature (Inconel® 690 melting point is 1345 °C), and not corrosion of the Inconel® 690.[12,13,21] It should be noted that several Inconel® 690 components in Melter #1, including the upper electrodes, have exhibited deflection similar to that observed in the SGM and IDMS.[21] During the metallographic inspection of the IDMS, an extensive change in the Inconel® 690 morphology was noted including internal void formation, extremely large grains, and grain boundary precipitates throughout the grain structure. These microstructural changes are from long term elevated temperature exposure[66] and effect the mechanical properties of the Inconel® 690, explaining the deflection of the electrodes.[21] Other possible causes of the deflection are increased convection in the melt pool, movement of the cold cap, or the thermal gradient in the top head components associated with the location in the melter relative to the dome heaters.[57]

5.2 DWPF Melter #2

In March 2003, DWPF Melter #2 began radioactive operations[12] utilizing a reducing flowsheet and is still in use today. The melter configuration described in section 2.1 is different after the installation of bubblers in September 2010.[12] These changes include replacing the outside thermowell with a dual purpose thermowell and bubbler, removing the center nozzle glass pump and installing just one modified feed tube, placing two bubblers in the nozzles previously used for the two feed tubes, and replacing the level probe with a dual purpose level probe/bubbler.[12]

In 2003, three samples of glass were taken from various places in the melter, specifically where deposits of crystallized glass were building up.[11] The deposits were building up in the upper pour spout bore and the pour spout riser insert while processing high waste loaded glass, which created a heat sink problem.[11] A discussion of those results related to the corrosion of Inconel® 690 is in section 6.1.2. Analysis indicated corrosion of the K-3 refractory was occurring at an rate too low to measure in Melter #2 at the time the samples were obtained.[11]

As part of preparations for processing Sludge Batch 3, static molten glass corrosion laboratory tests using anticipated glass chemistries were performed to evaluate the corrosion resistance of melter MOC (Inconel® 690) in vapor and molten glass regions.[42] Sludge Batch 3 contained a much higher sulfate and chloride concentration than previously processed sludge, which resulted in a higher molten glass corrosion rate.[42] During tests, pitting and evidence of sulfidation was observed in the Inconel® 690 off-gas lines.[42] Based on the results of the study, there was not a corrosion concern for processing Sludge Batch 3; however it was recommended that a comprehensive corrosion evaluation be performed to ensure safe chemistry limits for future melter feeds.[42]

In September 2010, bubblers were installed in Melter #2, which required changing the configuration of the top-head components. These changes included replacing the outside thermowell with a dual purpose thermowell/bubbler, removing the center nozzle glass pump and installing just one modified feed tube, placing two bubblers in the nozzles previously used for the two feed tubes, and replacing the level probe with a dual purpose level probe/bubbler.[12] Additional modifications included a new feed tube jumper that allows feeding from feed loop 2 only, a new electrical jumper for the feed jumper motor operated valve, a new feed tube flush water jumper and flexible cooling water jumper, and argon jumpers for the new bubblers.[12] This report focuses on the melter configuration prior to installation of the bubblers since at the time of this report, there is no data regarding the degradation of the Monofrax® K-3 or Inconel® 690 components post-bubbler installation.

6.0 Melter Lifetime

Multiple tests were performed to determine the best MOC for use in the DWPF Melter in order to determine the projected melter lifetime. As discussed in section 2.0, the materials compatibility program[3,4,18] used both laboratory-scale and pilot-scale tests to estimate the lifetime of the DWPF melter MOC. The literature suggests that the original basis for the two year melter lifetime was based on the average lifetime of commercial fiberglass melters at the time[2] as well as testing with the Project 1941 Melter.

A trip report detailing a visit from the Carborundum Company to SRL states "the refractories of the Project 1941 Melter had experienced much less corrosion than the commercial glass melters than normally seen.[2] However, it should be noted that the approximate operating temperature of the commercial fiberglass melters is 1370 °C – 1400 °C.[2] It is expected that the lifetime of this melter in waste glass production would be greater than two years".[2] In addition, Wicks states, "electric glass melters normally last about two years in commercial operations. Under special conditions, lifetimes have been extended to 3 and 4 years. For the melting of SRP glass-waste, the lifetime should be somewhat longer. Thus, the estimated lifetime of a defense waste melter is in the range of 2 to 5 years."[3] Owens-Corning Fiberglas (OCF) personnel noted "in OCF furnaces up to 8 inches of a 12 inch thick brick corrodes in approximately 3 years. The corrosion rate in OCF melter throats is up to 50 or 100 % higher and the increased rate is from upward drilling."[67]

In addition to the analysis of commercial melters at the time, the basis for the two year lifetime came from the refractory corrosion of the Project 1941 Melter throat (prior to the throat being lined with Inconel® 690). An average of 12 mils/day was observed (Table 4-1), and DuPont did not want half of the brick corroded (at the melt line) in two years. Coupon testing, discussed in section 3.0, confirmed the lifetime of the DWPF Melter was expected to be 2 – 6 years.[2-4] Based on the operational history of both DWPF Melters and the scaled melter testing, coupon testing with simulants provides a conservative estimate of melter lifetime.

Melter #2 was commissioned in early 2003 and has been in service for over 11 years operating with a reducing flowsheet ($Fe^{2+}/\Sigma Fe$ ratio of 0.09 – 0.33) with no major life limiting issues. Both Melters #3 and #4 are on-site with Melter #3 being completely assembled.

6.1 Melter Operation

6.1.1 Monofrax® K-3

Based on pilot-scale melter operating experience as well as examination of Melter #1, the area of highest refractory wear is at or slightly below the normal melt line.[8,21,26,30] As discussed in section 2.3, the pilot-scale melter testing showed no evidence that the Monofrax® K-3 refractory would not meet its two year design life.[8,10,12,13,50,52,53] However, data from the refractory corrosion from operation of the IDMS and other scaled melters would suggest that oxidizing feeds accelerate refractory corrosion as discussed in section 4.1.5.[8] This finding is verified though Jantzen's work at SRS indicating that a oxidizing flowsheet should be avoided in order to extend the lifetime of the DWPF Melter.[5,6] Melter #1 processed 105 tons of oxidizing feed during the cold start-up that accumulated two inches of deposits on the melter floor.[5,6] These deposits are attributed to Monofrax® K-3 corrosion while processing the oxidizing feed since the DWPF controls the melt pool liquidus temperature at a 100 °C margin below the nominal melt temperature of 1150 °C so that spinels forming from the melt are not present.[6] Comparing these results to the coupon testing discussed in section 3.1, oxidizing feeds are 1.8 – 2.8 times more corrosive to melter MOC than reducing feeds in non-agitated melters and coupon test conditions.[6] Melt agitation, based on commercial glass testing, increases the Monofrax® K-3 degradation since the saturated protective layer is removed from the bulk refractory and replaced by fresh glass melt.[5]

Therefore, as evidenced by the operation of Melter #1 for 8 years (approximately 3 years was under $Fe^{2+}/\Sigma Fe < 0.09$), as well as the continued operation of Melter #2 for more than 11 years (all operation between $Fe^{2+}/\Sigma Fe$ 0.09 – 0.38), HLW waste melter lifetime based on Monofrax K-3 refractory degradation can be significantly longer than the anticipated 2 – 6 years. Since testing of the Monofrax K-3 refractory in oxidizing feeds is 1.8 – 2.8X more aggressive than reducing feeds,[5,6] the longevity of the DWPF melters is, in part, due to the compatibility of a reducing melter feed with a highly reduced refractory.

6.1.2 Inconel® 690

Multiple inspections of the Inconel® 690 components were performed during the pilot-scale testing. Given that the DWPF pour spout bore down to the glass disengagement point at the bottom of the insert are more oxidizing and at a lower temperature than the melt pool, there is a propensity to nucleate spinels on the Inconel® 690 surfaces in this region. This is especially the case with higher waste loaded glasses as this region is a heat sink for the glass.[11] Prior to the addition of a heater below the pour spout insert in Melter #2, it was difficult to maintain a high enough temperature in this region to prevent spinel formation, while not oxidizing the Inconel® 690 heaters, as well as stabilize the molten glass stream. As a result, insulation was added to the pour spout, the bellows were heated, and thermocouples were repositioned, which increased the lifetime of the heating elements.

The localized oxidative corrosion of Inconel® 690 provides excess Cr_2O_3 nuclei that can act as heterogeneous nuclei for spinel growth in the region of the pour spout bore as evidenced in Melter #2. The oxidative corrosion of Inconel® 690 and the insufficient heat in the pour spout is consistent with the operating history of the LSFM, which had a pour spout temperature of ~1075 °C, poured lower waste loaded glasses, and did not experience any pour spout pluggages.[11] This phenomena is also consistent with the pour spout pluggages experienced during the first campaign with the SGM when the pour spout tip was 980 °C.[11] Once the SGM pour spout was better insulated and the thermocouple locations redesigned, the SGM was able to pour glasses with calculated waste loadings up to approximately 42 wt %.[11]

In 2003, three glass samples were taken from Melter #2 after the waste loading had been increased to nominally 38 wt%.[11] Analysis of deposits in the Melter #2 pour spout showed elevated concentrations of Cr_2O_3 as well as nickel iron spinel ($NiFe_2O_4$).[11] It is hypothesized that the protective chrome oxide layer on the Inconel® 690 spalls off from a combination of the dynamic glass pouring environment, the oxidation profile in the pour spout, and the cooler pour spout temperatures (800 - 1050 °C).[11] This combination allows the freshly exposed NiO-rich Inconel® 690 surface to react with the Fe_2O_3 in the waste glass, initiating spinel crystalization.[11] It was not clear from the analysis if higher waste loading had an effect on the deposits in the pour spout; however based on the presented hypothesis, increasing the Fe_2O_3 concentration could increase spinel crystallization. In addition, the pour spout is a heat sink and the glass was at or below the liquidus temperature, which would lead to deposits in the pour spout.[11] The samples from Melter #2[11] and testing with the SGM and LSFM[10] support the importance of controlling the pour spout temperature and environment, as well as the waste glass composition, to reduce the corrosion of the Inconel® 690 and prevent unwanted deposition/crystallization.

Various degrees of degradation were observed on the Inconel® 690 Melter #1 top head components during the non-radioactive DWPF operation.[34] Both the melter feed tube and the borescope failed, but the dome heaters were in excellent condition, since they only experience oxidation. More severe attack occurred in specific temperature regions (500 °C to 650 °C) of the melter vapor space and melter top head components.[34] Chloride and sulfate bearing compounds present in the off-gas condense and concentrate on the colder melter top head components and break down the protective chromium oxide layer, resulting in severe degradation of the metal substrate.[34]

The melter feed tube failure was attributed to three main causes: 1) exposed end grains at the end of the tube which are more prone to attack than long or equiaxed grains, resulting in more exposed grain boundary area and more channels for chromium diffusion, 2) the outer jacket was water cooled so the temperature was in the 500 – 650 °C range, and 3) sulfate and chloride salts deposited on the cooler surface, corroding the Inconel® 690. The solution was to weld overlay the end grains which reduced the degradation such that no further redesign was necessary.[34,57]

Borescope failure was similar to feed tube failure. The borescope outer housing was swept with air to cool the camera and to force air out the end to keep particles of glass from coating the camera lens. In addition, a periodic steam purge was used to clean the lens.[57] The main causes were: Inconel® 690 (prone to attack), air cooling kept the outer housing in the 500 to 650 °C temperature range, sulfate and chloride salts condensed on surface, steam purge shocked protective oxide off, and the air in the plenum that was forced through the outer housing promoted rapid oxidation. Ultimately, the borescope failed and was attributed to molten salts and oxidation since it was in the region where the temperature was just right for sulfur and chloride containing compounds to condense and attack.[34,57] If there were no salts, the attack would probably not have been as severe but the oxide layer would still have spalled off with the steam purge.

Visual inspection of other melter top head components, including the dome heaters in Melter #1 after it was shut down, showed they were in good condition.[21] There was no significant deflection and no visual indication why the one set had failed. The dome heaters are constantly operated at 950 °C, which allows the formation of a stable protective oxide. The higher temperature also prevents salts depositing on the metal surface.[34,57] Based on DWPF Melter operations, the corrosion of the Inconel® 690 components was no more severe than predicted by laboratory and pilot-scale melter testing.[21] Problems only existed in localized regions that were exposed to very specific conditions (materials and environment) that were outside laboratory conditions.

7.0 Conclusion

A glass melter for use in processing radioactive waste is a challenging environment for the materials of construction (MOC) resulting from a combination of high temperatures, chemical attack, and erosion/corrosion; therefore, highly engineered materials must be selected for this application. The focus of this report is to review the testing and evaluations used in the selection of the Defense Waste Processing Facility (DWPF), glass contact MOC specifically the Monofrax® K-3 refractory and Inconel® 690 alloy. The degradation or corrosion mechanisms of these materials during pilot scale testing and in-service operation were analyzed over a range of oxidizing and reducing flowsheets; however, DWPF has primarily processed a reducing flowsheet (i.e., $Fe^{2+}/\Sigma Fe$ of 0.09 to 0.33) since the start of radioactive operations. This report also discusses the materials selection for the DWPF off-gas system and the corrosion evaluation of these materials during pilot scale testing and non-radioactive operations of DWPF Melter #1. Inspection of the off-gas components has not been performed during radioactive operations with the exception of maintenance because of plugging.

Development of the current DWPF glass melter and off-gas configuration dates back to 1976, when work began on the first prototype melter system. From 1976 – 1994, five pilot-scale melters were tested to verify and improve the design of the DWPF Melter. During that time, laboratory-scale testing of the two main glass contact materials, Monofrax® K-3 and Inconel® 690, that impact melter life was also performed.[3,4,18] Based on the results of the laboratory coupon tests, the lifetime of the DWPF Melter was expected to be 2 – 6 years.[2-4] The pilot scale melter testing confirmed the two year life of the melter and results indicated the melter lifetime could be extended past the two year design basis.

During this same time period, laboratory and scaled tests were performed in order to rank and ultimately select Inconel® 690, Hastelloy® C-276, Allvac® Allcorr®, and Type 304L SS for the DWPF off-gas system components.[27] The results of the off-gas MOC coupon tests were confirmed by the corrosion evaluation of the IDMS[15-17,60] as well as MOG inspections after the DWPF Melter #1 non-radioactive runs.[40,64] Although there have been several pluggages of the off-gas system, corrosion does not limit the lifetime of the off-gas components, which was estimated at 2 – 5 years.[34,61,62,64] The original melter off-gas components are still functioning after over 18 years of non-radioactive and radioactive operations, indicating the predicted lifetime for MOG system components is overly conservative.

Various degrees of degradation were observed on Melter #1 Inconel® 690 top head components during the approximate two year non-radioactive DWPF operation (oxidizing melt pool, $Fe^{2+}/\Sigma Fe \sim 0$), with the most severe attack occurring in the hotter regions of the melter vapor space on air or water cooled melter top head components. This attack was attributed to chloride and sulfate bearing compounds present in the off-gas condensing and concentrating on the colder melter top head components, thus breaking down the protective chromium oxide layer and degrading the metal substrate of the Inconel® 690. Prior to radioactive operations of Melter #1, the most susceptible Inconel® 690 components were altered by a weld overlay to extend their lifetime to meet the two year design life. For the Monofrax® K-3 refractory, operation of Melter #1 confirmed the results of the pilot scale melter testing showing the area of highest refractory wear is at or slightly below the normal melt line. DWPF Melter #1 was shut down after eight years of operation; however, the Monofrax® K-3 refractory and Inconel® 690 components were still in relatively good condition, indicating the melter lifetime was not limited by the glass contact MOC.

DWPF Melter #2 continues to operate after 11 years with a reducing flowsheet ($Fe^{2+}/\Sigma Fe$ ratio of 0.09 – 0.33), further reinforcing that the original two year design basis for DWPF Melters is overly conservative based on 11 years of radioactive operations.

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Appendix A. Pilot Scale Melter Configurations

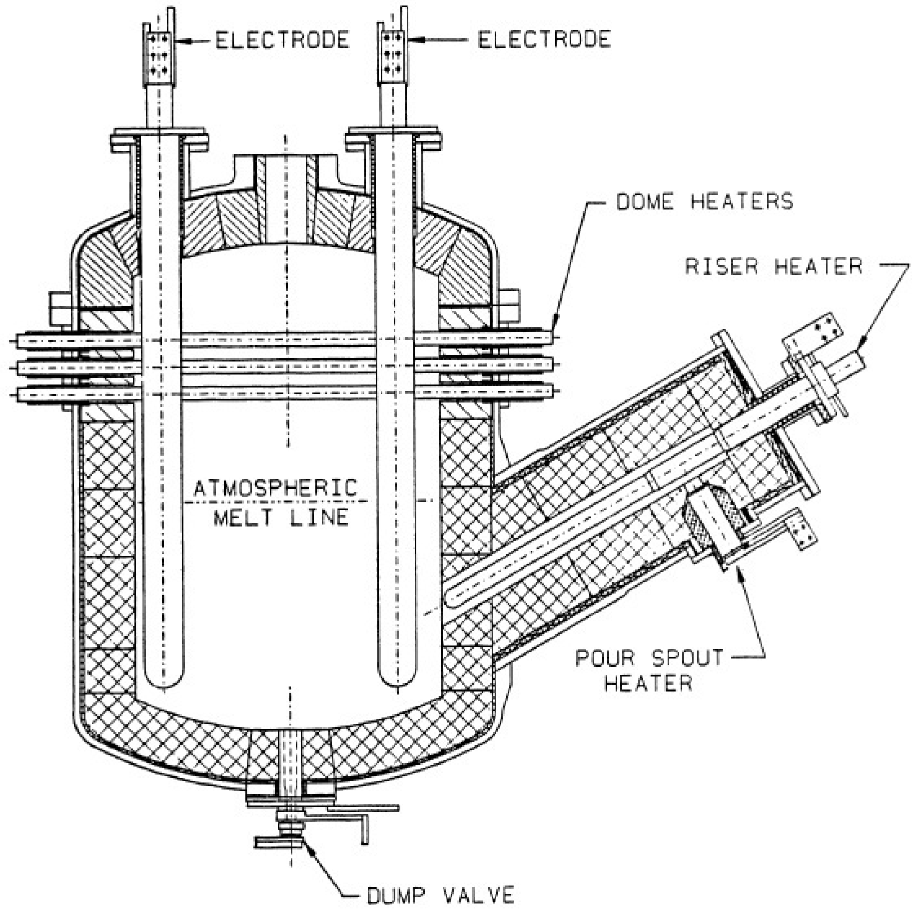

Figure A-1. Cross-sectional view of the Project 1941 Melter.

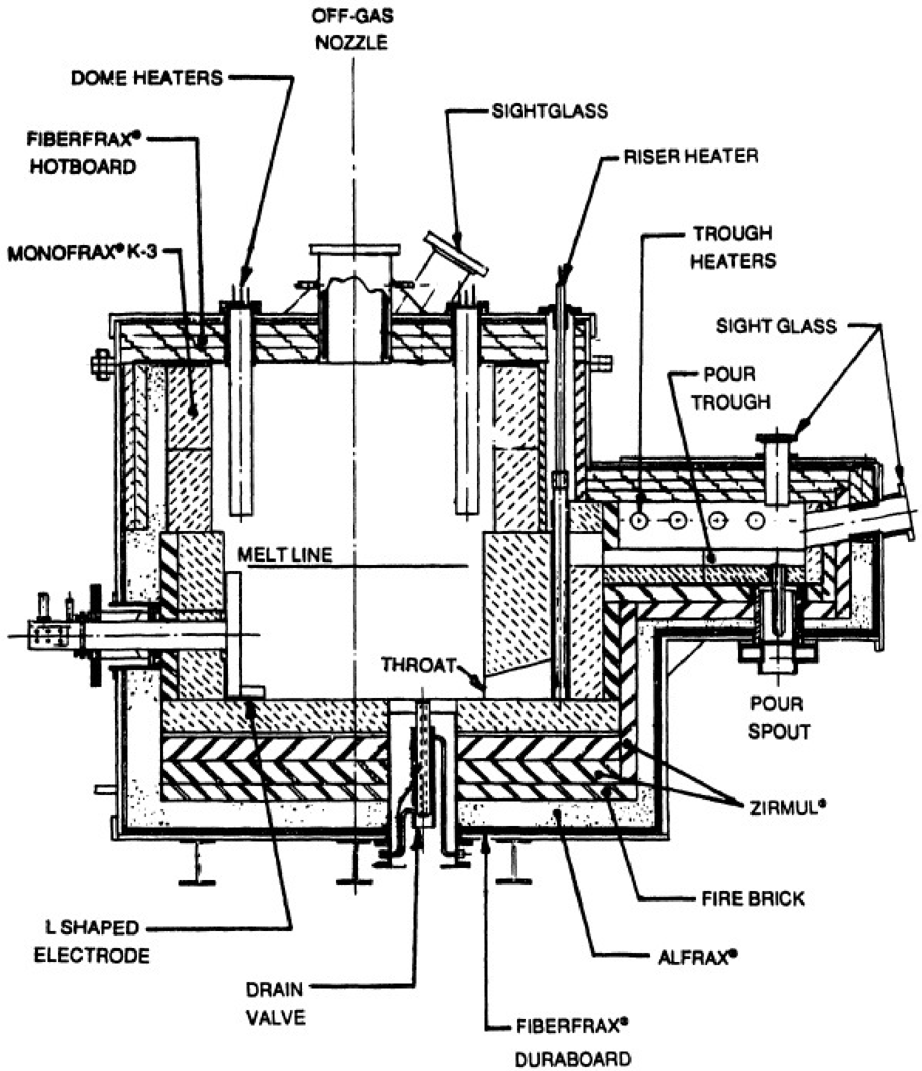

Figure A-2. Cross-sectional view of the LSFM.

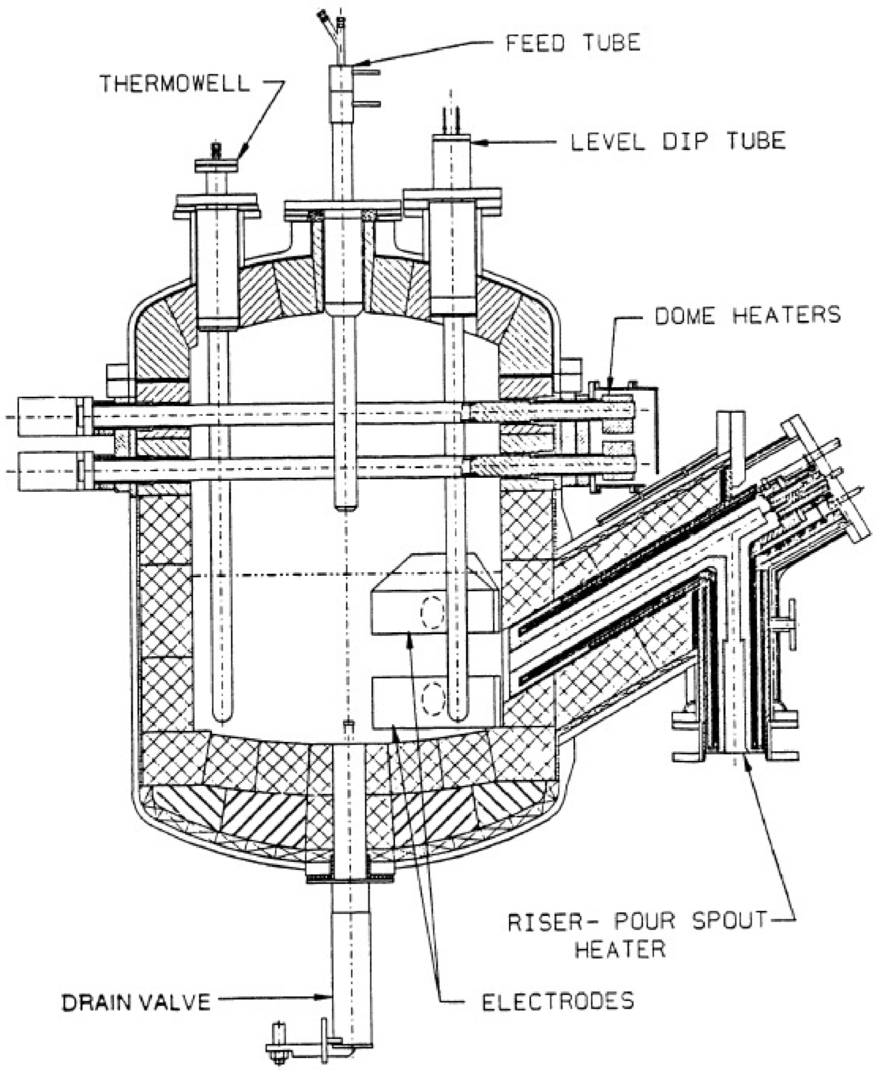

Figure A-3. Cross-sectional view of the Scale Glass Melter.

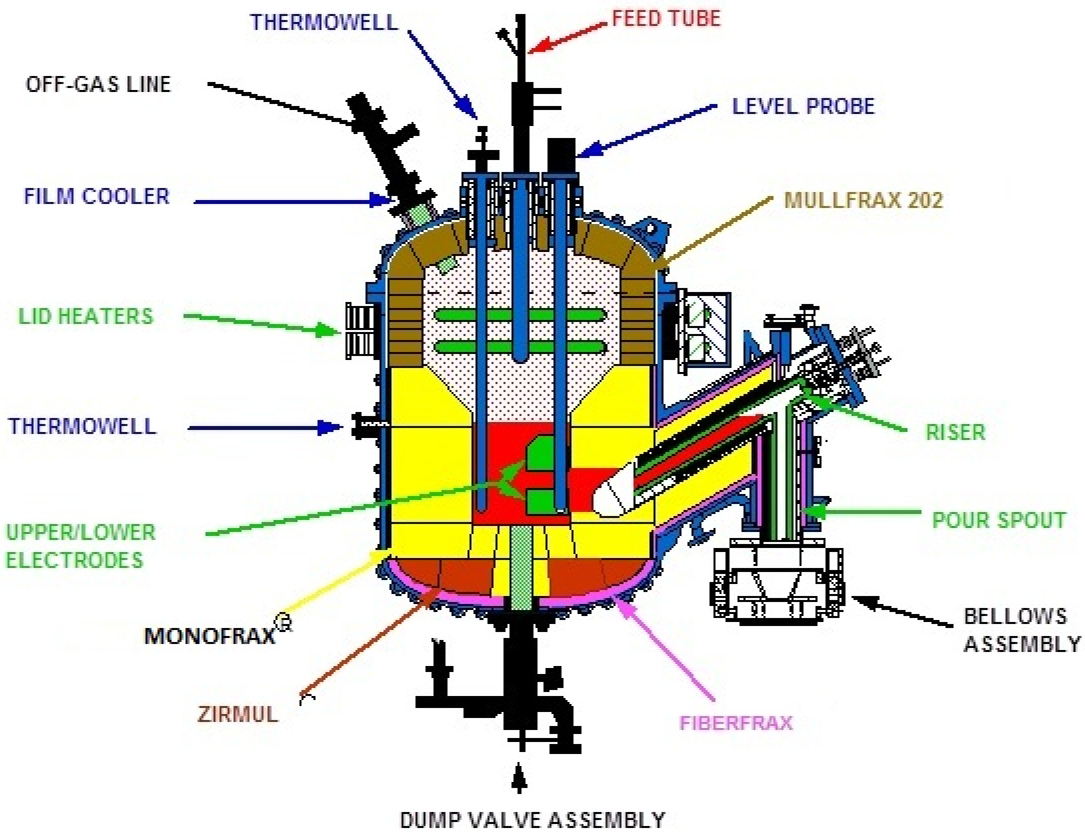

Figure A-4. Cross-sectional view of the IDMS.

Distribution:

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J. H. Christian, 999-W
A. S. Choi, 999-W
D. H. McGuire, 999-W
S. D. Fink, 773-A
K. M. Fox, 999-W
C. C. Herman, 773-A
E. N. Hoffman, 999-W
K. J. Imrich, 773-A
D. C. Iverson, 704-30S
C. M. Jantzen, 773-A
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