OVERVIEW - DEFENSE WASTE PROCESSING FACILITY OPERATING EXPERIENCE

Michael R. Norton, Hasmukh B. Shah, Michael E. Stone, Larry E. Johnson, Richard O'Driscoll
Westinghouse Savannah River Company, Aiken, SC

ABSTRACT

The Savannah River Site's Defense Waste Processing Facility (DWPF) near Aiken, SC is the world's largest radioactive waste vitrification facility. Radioactive operations began in March 1996 and over 1,000 canisters have been produced. This paper presents an overview of the DWPF process and a summary of recent facility operations and process improvements. These process improvements include efforts to extend the life of the DWPF melter, projects to increase facility throughput, initiatives to reduce the quantity of wastewater generated, improved remote decontamination capabilities, and improvements to remote canyon equipment to extend equipment life span.

This paper also includes a review of a melt rate improvement program conducted by Savannah River Technology Center personnel. This program involved identifying the factors that impacted melt rate, conducting small scale testing of proposed process changes and developing a cost effective implementation plan.

INTRODUCTION

The Defense Waste Processing Facility (DWPF) began radioactive operations in March 1996. The purpose of DWPF is to immobilize approximately 37 million gallons of high level radioactive waste currently stored in underground tanks at the Savannah River Site (SRS). The high level waste is vitrified into a durable borosilicate glass, poured into stainless steel canisters, and stored prior to eventual disposal in a geologic repository. DWPF has produced 1,178 canisters of high level waste glass as of October 1, 2001. This represents 20% of the total canisters required to immobilize all of the SRS high level waste in the underground tanks.

Prior to radioactive operations, the DWPF completed a Waste Qualification Run using various compositions of simulated waste. The extensive characterization of the glass and canistered waste form demonstrated that the DWPF complied with the Department of Energy's Environmental Management Waste Acceptance Product Specifications (WAPS). (1) Characterization of the canistered waste form in accordance with the program described in the DWPF Waste Form Qualification Report has continued to demonstrate compliance with the WAPS for all of the waste glass produced.

Numerous improvement initiatives have been implemented in the DWPF operation since the initiation of radioactive operations. These have included efforts to increase throughput, reduce waste generation, and extend equipment life span.

PROCESS/PRODUCT OVERVIEW

Most of the high level waste stored at SRS is a complex mixture of chemical and radionuclide waste generated during the acid-side separation of special nuclear materials and enriched uranium from irradiated targets and spent fuel in the SRS Separations Canyons. Of the 37 million gallons of high level waste in storage, approximately 3 million gallons are sludge waste and 34 million gallons are salt waste. The sludge waste, which is insoluble and settles to the bottom of a waste tank, generally contains insoluble radioactive elements including strontium, plutonium, americium, and curium in the form of metal hydroxides. The salt waste, which is soluble and is dissolved in the liquid rather than settling to the bottom of the waste tanks, contains most of the soluble radioactive element cesium. The salt supernate and dissolved salt cake removed from the waste storage tanks will be processed to remove the radioactive cesium. The cesium contains approximately 99.99% of the radioactivity in the salt waste, but is only a small fraction of the volume. The process for removing the cesium from the salt waste is currently under development and projections are for a new facility for this purpose to be operational in FY10. The decontaminated salt solution will be mixed with cement, flyash and slag. The resulting grout is classified as low level waste and disposed of by pumping it to engineered concrete vaults and allowing it to cure.

The current operations at DWPF involve vitrifying the sludge waste from the underground storage tanks. Current projections are that 5,914 canisters will be required to vitrify all of the current inventory of high level waste. DWPF is expected to operate with a "sludge–only" flowsheet until FY10 when the salt processing facility is projected to be operational. Approximately 52% of the total canisters produced will contain sludge only waste, and 48% of the total canisters will contain sludge and salt waste (coupled operations).

The sludge waste is washed in an underground storage tank to remove soluble salts, primarily sodium. The sludge waste is sampled and the sample is characterized and processed into borosilicate waste glass to ensure that the requirements of the WAPS are met. DWPF is currently completing processing of the second batch of sludge from the underground waste tanks. The depletion of this sludge batch is projected to be in December 2001. The characterization of the third sludge batch is in progress. The quantity of canisters produced and some of the canistered waste form properties for these sludge batches are shown below.

Table I: DWPF Canister Production Data

	Macrobatch #1 Sludge Batch #1A (complete)	Macrobatch #2 Sludge Batch #1B (in progress)	Macrobatch #3 Sludge Batch #2 (projected)	Design Basis Coupled Operations
curies/canister	820	5100	6300	234,000
rem/hr at 30 cm	3	6	10	2400
watts/canister	6	26	25	690
canisters poured	495	700	500	---

The sludge waste is transferred into the Sludge Receipt and Adjustment Tank (SRAT) in the DWPF. The sludge waste is treated with formic acid to remove mercury, neutralized with nitric acid, and concentrated. The SRAT product is transferred to the Slurry Mix Evaporator (SME). The SME process includes the addition of a borosilicate glass frit and additional concentration. The SME contents are sampled to verify that the waste glass will meet the quality requirements. The amount of sludge waste from the SRAT and the amount of glass frit are tightly controlled in order to produce the proper blend which will yield a waste glass that meets the WAPS.

The SME is the primary hold point in the process. The samples from the SME are analyzed to ensure that the resulting waste glass will meet the WAPS requirements. The WAPS are divided into five sections: wasteform (borosilicate glass), canister, canistered waste form, quality assurance, and documentation. The most important of the glass specifications is the product consistency specification which states that DWPF must control its process so that the waste glass produced is more durable (resistant to leaching) than the DWPF Environmental Assessment Glass as measured by the Product Consistency Test (PCT). The PCT is a crushed glass durability test in which the results are expressed as the amount of boron, lithium, and sodium measured in the leachate. The DWPF glass property model uses the SME composition to predict the leach rates. Acceptance of the waste glass is based on this prediction. The SME product is verified to be acceptable before it is transferred into the Melter Feed Tank (MFT). A waste glass sample is taken occasionally while a canister is being filled to confirm that the glass durability as determined by a PCT is acceptable.

The melter feed material in the MFT is transferred to the melter. The molten waste glass is vacuum poured into a canister. After the canister is filled, a temporary seal is installed to prevent free liquid from entering the canister during the decontamination process. Decontamination of the canister surface consists of blasting an air injected frit slurry against the canister. The spent frit slurry from the decontamination process is used in the next SME batch as part of the required frit addition. The canister is then welded closed and transferred to an interim storage building.

MELTER OPERATION

The melter assembly consists of a cylindrical vessel internally lined with refractory brick and ceramic insulation and surrounded by a water-cooled jacket. The melter has a cylindrical riser originating near the bottom of the vessel that is inclined upwards for approximately 4 feet, where it is connected to a pour spout running vertically downward. The pour turntable holds four canisters and rotates to place a canister directly under the pour spout. Each canister holds approximately 3,800 lbs of glass. An array of auxiliary components is mounted on the dished head of the melter, including feed tubes, thermowells, a level dip tube and off-gas coolers. The feed from the MFT is pumped down feed tubes into the melter. The feed stream is heated with dome heaters mounted in the top head of the melter and then by two pairs of electrodes in the melt pool. Liquid is evaporated from the feed slurry which is calcined and melted. The molten glass is drawn up the riser via a vacuum system and flows down the pour spout into a canister. A metal bellows assembly is expanded to provide a seal between the canister and the bottom of the pour spout.

Several months after DWF initiated radioactive operations, problems developed with the stability of the glass pour stream which caused the stream to wick and migrate from the intended release point of the glass at the upper knife edge of the pour spout. This wicking process produces an accumulation of glass in the lower pour spout and bellows area that required frequent shutdowns for cleaning. It was eventually determined that the cause of the wicking was the degradation of the pour spout due to erosion from the flow of glass over time. The glass stream passes over the top of the pour spout, down the side of the pour spout until it reaches the upper knife edge. The glass should disengage from the pour spout wall at this knife edge and free fall into the canister. As the pour spout aged, the glass stream eroded away this knife edge and the lower knife edge, so that the glass preferentially flowed down the pout spout wall and did not properly disengage. This resulted in significant problems with glass accumulation in the bellows and the lower pour spout that prevented the pour stream from entering the canister.

The pour spout is an integral part of the melter and cannot be replaced without replacing the entire melter. Replacement of the DWPF melter would have required a six month outage and significantly impacted the processing of the high level waste at SRS. The resolution of this problem involved the development of a remoteable pour spout insert. This insert is an Inconel sleeve that is installed into the pour spout and mates up with the remaining portion of the upper knife edge. The insert provides a replaceable knife edge to allow the glass pour stream to properly disengage from the pour spout wall and flow into the canister.

The development of a telerobotic manipulator (TRM) was instrumental in the facility's ability to recover from the pour spout degradation. The TRM is used to clean the bellows and lower pour spout area when required. It is also used to install and remove the inserts into the pour spout. The TRM is also used for various cleaning and inspection tasks in the melt cell.

The DWPF melter uses cooling water in several locations to cool the shell of the melter and other melter components. One of these components is the bus bars which connect the melter dome heater transformers to the dome heater electrodes. These bus bars are cooled in order to prevent warping which would impact the quality of the electrical connection. Cooling water flows through copper tubing which is welded to the bus bars. In July 1999, cooling water leaks developed at several locations in the copper tubing. The failure mechanism is believed to be stress cracking due to thermal cycling. The cooling water leaks could potentially cause the transformers to fail or loss of cooling could have impacted the electrical connection between the busbars of the transformers and the dome heater tubes. Actions were taken to minimize the leakage rate, while a resolution was developed. The cooling water lines that required repair are an integral part of the melter and the repair methodology needed to be implemented with the melter installed in the canyon. The development of a method to repair the copper tubing was initiated. Various external repair methods and internal sealants were tested. The methodology that was developed involves the application of a commercially available automotive radiator sealant. An application rig was designed, tested and used for the repair activities in the facility. This sealant requires periodic reapplication in order to maintain the cooling water leakage to an acceptable rate. An improved bus bar design has been developed for future melters which will significantly reduce the risk of a cooling water leak.

The development of solutions to these problems and other melter operating problems has allowed the DWPF melter to exceed the expected design life by over 5 years. Since a melter replacement outage is estimated to require six months and a replacement melter costs approximately $25 million, resolving these problems has significantly impacted our ability to process the high level waste at SRS.

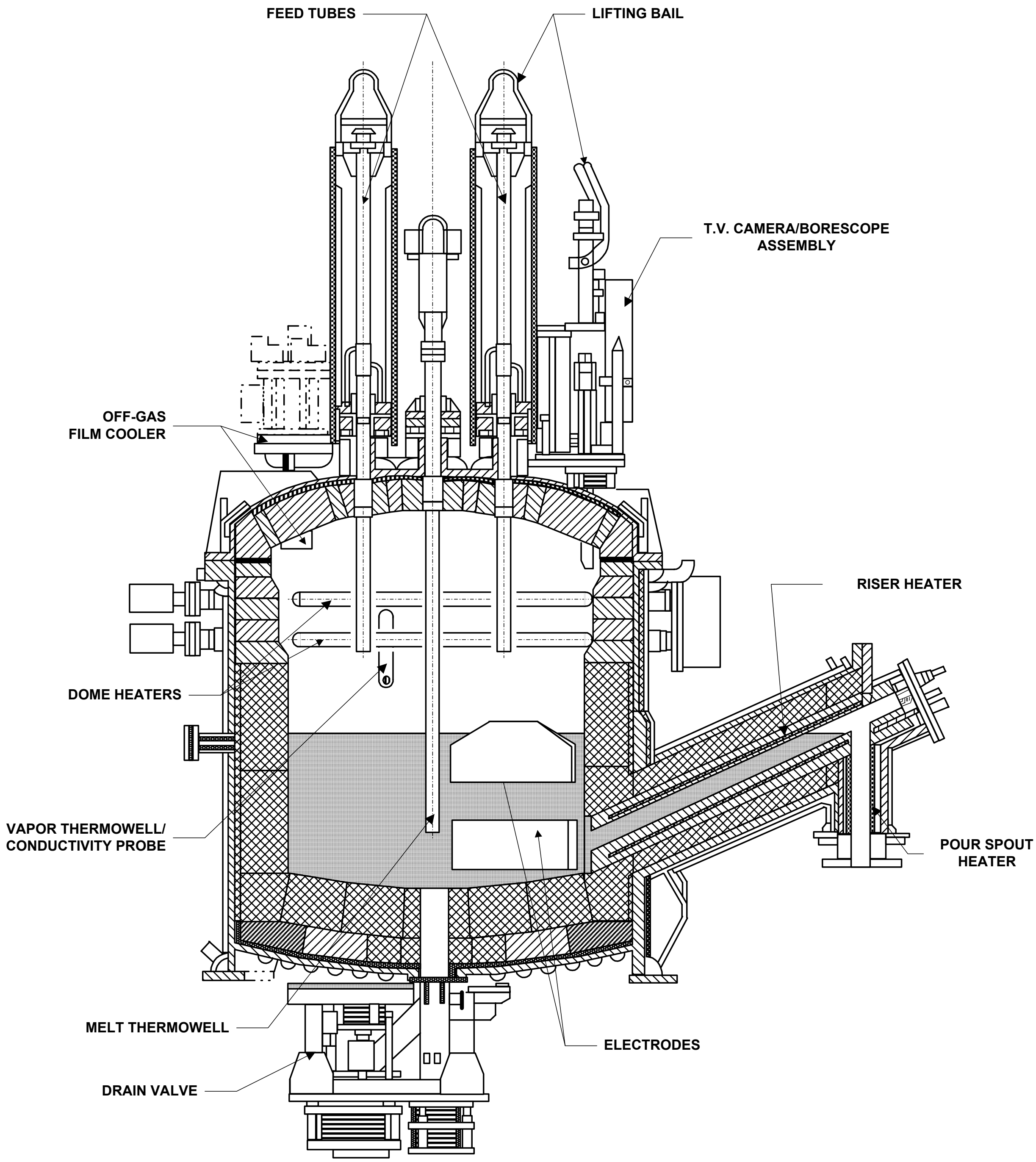
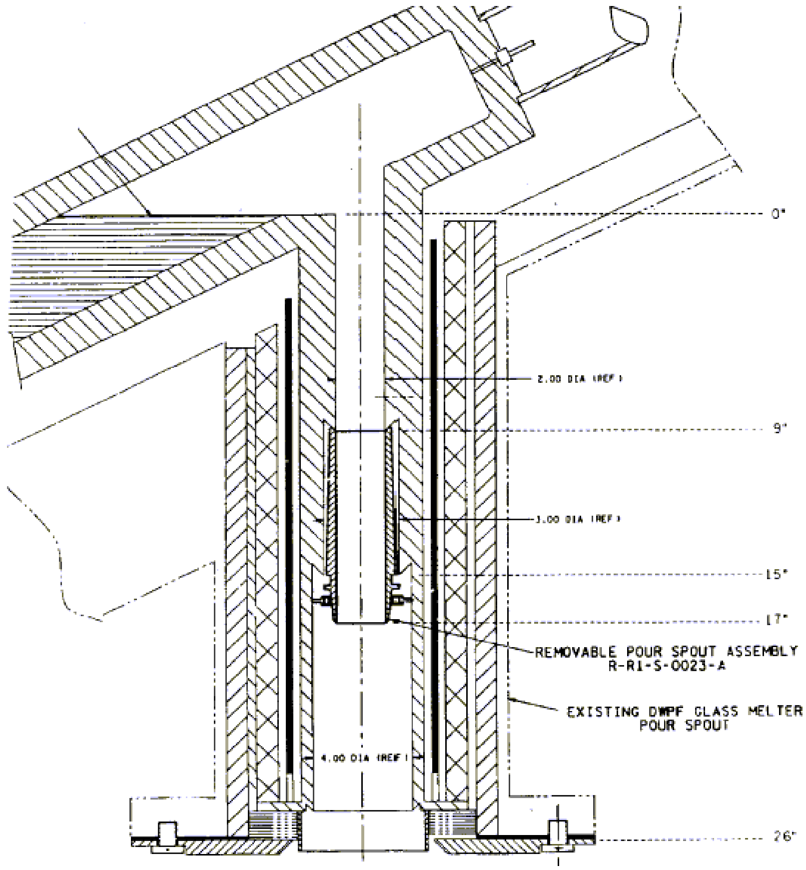


Fig. 1. The DWPF Melter



Detail of the Insert

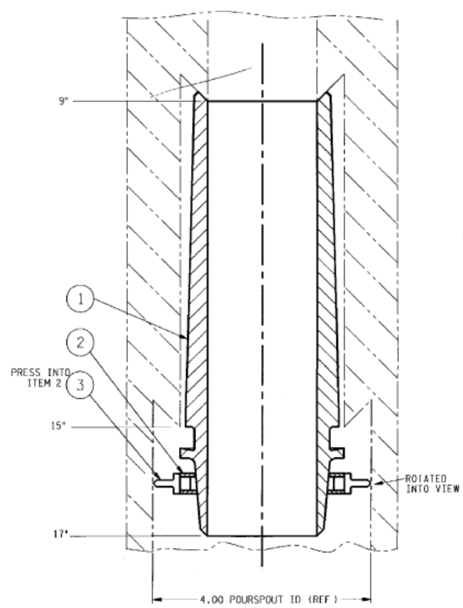


Fig. 2. The Melter Pour Spout Showing the Replaceable Insert

DWPF THROUGHPUT IMPROVEMENTS

Several throughput improvements have been implemented since the initiation of radioactive operations. One of the factors that impact the melting rate in the melter is the water content of the feed slurry. The evaporation of the water from the feed slurry requires heat which is not available to melt the slurry. Several operating changes and equipment modifications have decreased the water content of the feed slurry. These have included reducing sample pump priming timers, modifying the operation of the feed pumps, reducing the quantity of flushing for the MFT sample lines, and closely monitoring the MFT water content and adjusting the SME product water content as needed.

Several process changes have been implemented which either provide more heat to the melter or reduce the amount of heat loss from the melter. These have included the reduction of air inleakage in the melter. Air inleakage carries heat away from the melter and reduces melt rate. The melter flammability models were enhanced with additional data from the development melters. The new model allowed the flammability controls to be revised. The modification of the flammability controls for the vapor space of the melter has allowed lower vapor space temperatures to be maintained in the melter. This has allowed a higher feed rate while still keeping the vapor space of the melter well above the lower flammability limit.

WASTEWATER REDUCTIONS

Modified Off Gas Operation:
The design flow path of the off-gas system is through the film cooler : quencher : OGCT: SAS Stage #1 : SAS Stage #2 : Condenser : HEME Filter : HEPA Filter : Off-Gas Exhauster : Zone 1 Exhaust tunnel : Sand filter : Zone 1 Exhaust Fans and then the stack.

In an effort to reduce the volume of recycle wastewater transferred from DWPF to the tank farm, while the evaporator was out of service, an engineering study was performed to consider the impact of isolating the steam to the SAS stages. The reduced wastewater generation would be offset by decreased Decontamination Factor (DF) for the off-gas system and an increased particulate loading on the HEME filters causing not only increased frequency of change out, but loss of production during the changeout time period. In addition, dissolution of the HEME filters would add caustic and siliceous recycle to the evaporator. Environmental Compliance Group and DOE approvals were obtained prior to implementation of the plan.

Isolating the flow of Steam to both SAS stages reduced the recycle wastewater to the tank farm by 2,000 gallons per day or 730,000 gallons per year. The DF of the off-gas system was calculated to be decreased by a factor of fifty, from 8.0×10^8 to 1.6×10^7. This is acceptable for sludge only operations.

Sampling of stack emissions is normally conducted once a month. The sample frequency was increased to weekly and gradually reduced to the original monthly sample after a number of weeks of analysis showed there was negligible impact on the DWPF emissions.

Particulate matter, which had previously been removed from the off-gas stream by the steam scrubbers, is now collecting on the HEME filters. Engineering monitors and trends the pressure drop (DP) across the HEME filter to ensure they are replaced before the DP becomes too large. The increased particulate loading has required the HEME filter elements to be changed about every six months, compared to no change outs during the first five plus years of operation. There are three filters per HEME assembly. The dissolution of the HEME filters in a caustic solution has yet to be performed. It is estimated that at least six filter elements, representing about a year of service, can be dissolved in about 5,000 gallons of liquid which will be returned to the tank farm as more recycle waste.

This waste will contain more caustic and siliceous material than normal. In addition, it requires about two days worth of down time per change out, or four days of potential glass production per year. This equates to approximately four canisters per year of decreased production capability.

Each new sludge batch sent to DWPF while the SAS are out of service will require increased sampling for emissions during the first few weeks to months. It is recommended that the SAS be returned to service once the tank farm wastewater space has been caught up after the 2H evaporator is returned to full service.

CDC Water Reductions:
The CDC uses an air-injected frit slurry blasting process to decontaminate the canister exterior surface. The process is controlled by a PLC and consists of a 108 step decontamination sequence that blasts and rinses the canister and grapple, rinses the chamber, and dries the canister and chamber. The CDC process produces a large volume of spent frit and water, which is, transferred the Slurry Mix Evaporator (SME) during the canister decontamination process. Calculations indicated that approximately 1500 to 1600 gallons of spent frit slurry were transferred to the SME for every canister decontaminated. This volume of spent frit slurry was calculated to contain approximately 250 gallons of decon frit slurry, 1000 gallons of rinse and flush water, and 350 gallons of pump prime water. Decreasing the volume of decon frit slurry, flush, rinse, and prime water was studied to decrease both the SME processing time and the liquid waste volume returned to H-Area Tank Farm.

Several items were identified. The list below represents the major changes.

The canister re-cleaning control logic was modified to allow the operator to restart the automatic decontamination sequence at intermediate steps instead of restarting at the beginning of the sequence after a control system abort or when there is incomplete canister cleaning.
CDC system operating manual was revised to reduce the maximum number of transfer pump starts from 3 to 1.
The CDC control system was replaced, improving overall system reliability and eliminating many unnecessary alarms. The improved performance has reduced the number of automatic sequence aborts; therefore the spent frit volume has been reduced by reducing the number of times that canister re-cleaning is required after an abort.
The Decon Fit Slurry Feed Tank agitator blades were replaced which improved decon frit slurry mixing and nozzle feed pump reliability. Incomplete canister cleaning has been reduced which has reduced the number of times that canister re-cleaning is required.
The CDC automatic sequence with the chamber rinse was isolated.

The potential water reduction from the successful implementation of these items was between 300 to 400 gallons per canister. This amounts to about 75 to 90,000 Gal/yr water reduction.

FRIT Slurry make-up System Water Reductions:
The frit is processed to the Frit Weight Bin until the desired weight for the batch is reached. The frit weigh bin screw conveyer normally feeds the batch of processed frit to the Frit Slurry Make up Tank (FSMUT). The available spent frit from the Canister Decontamination System is added first to the SME. The remaining additional frit required is added as fresh frit slurry from the Process Frit Slurry Feed Tank (PFSFT). The frit slurry is pumped from the FSMT to the PFSFT. Usually, three FSMT transfers are required per SME batch.

The FSMT produces a 50 wt % frit slurry by mixing the frit with dilute formic acid. Before implementation of the once through processing, approximately 2300 gallons of water was used per one FSMT load. In once-through processing, FSMT is flushed and pumped at the same time to the PFSFT. Better insight is gained in how long tanks are flushed and how much water is used that has enabled to realize this gain. Since implementation of once-through processing, the water usage has been reduced from 2300 gallons to 1900 gallons per one FSMT load. This reduction translates to about 231 gallons per canister, and approximately 55,000 Gals/year.

WASTEWATER REDUCTION – CO_2 Decon:
Canyon equipment requiring repair is brought into the Remote Equipment Decon Cell (REDC) for decontamination prior to placement in the Contact Decon Maintenance Cell (CDMC). REDC operations are performed remotely, to prevent radiation exposure to personnel, utilizing a combination of the canyon's bridge crane, Master-slave manipulators, and two electro-mechanical manipulators (EMM). After staging in the CDMC, Maintenance personnel may enter to repair the equipment.

Equipment decontamination in the REDC is performed using spray wands directed by the EMMs. The decon solution normally supplied to the wands is a mild nitric acid solution aspirated into a steam or water/steam eductor. The cleaning fluids collect in the REDC sump, and become waste that has to be treated (neutralized) and pumped to the Tank Farm. For a large piece of equipment, the amount of waste generated can be substantial. To reduce this waste stream, DWPF installed and began using a CO_2 pellet blaster system in 1998. This system uses plant air to accelerate small dry ice pellets, which sublime upon impact with the surface being cleaned. The kinetic energy plus the "explosion" of the pellet lifts the material adhering to the surface. The only by-product is CO_2 gas, which is swept out through the building's ventilation system, and the contaminate itself. The CO_2 system is now used for the bulk of equipment decon. The liquid/steam systems are only used if radiological surveys or experience with the equipment in question indicate that more aggressive cleaning with acid is required.

CANYON EQUIPMENT IMPROVEMENTS

Agitators

Agitator shaft blades in the frit containing process vessels, Melter Feed Tank (MFT) and Slurry Mix Evaporator (SME), have shown to be susceptible to severe erosion wear. Thorough holes and deep pits developed in less than two years of operation. The agitators have two sets of blades; a three-bladed hydrofoil located about mid-elevation in the tank, and a four-bladed paddle type set located just off the bottom of the vessel. Originally the assemblies were fabricated entirely from Hastelloy C-276. A couple of different variations (configurations) of Stellite 6 weld overlays were applied to high wear areas of the blades with somewhat limited success. Recently two assemblies were installed that have blades fabricated from Ultimet® (Haynes International trademark) while the shaft remains C-276. Ultimet is a high Cobalt alloy that has similar corrosion resistance properties to C-276 and hardness close to Stellite. These units currently are approaching one year of operation, and are still under evaluation. However, based on lab data and some limited in-service data using this material as patching in small high wear areas of the heating/cooling coils (see below), substantial improvements in equipment life are expected.

Coils

The removable heating/cooling coils assemblies in the MFT and SME are also subject to erosion attack from the frit laden process fluid. Several repairs were made to this equipment during the first three years of operation (Cold Runs and Rad Ops). Areas of heaviest attack were always in the lower sections, which are near the tips of the lower agitator blades. Modifications made during the repairs included adding additional material for "erosion allowance", adding hardfacing material (Stellite weld overlay or Ultimet® coverplates), and changing geometry of the piping. The lessons learned were applied to an available spare coil as practical, and to a greater extent to two new spare coil assemblies purchased in 1999. The modified original spare and one of the new spares have been used in the facility, but have not been inspected since installation. The last failures (leak) were experienced in the SME in 1998 and in the MFT in 2000.

MELT RATE IMPROVEMENT WORK

Melt Rate Testing (2,3)

The Savannah River Technology Center (SRTC) conducted tests to assess potential alternative processing options to the DWPF flowsheet to improve melt rate for sludge batch 2 (DWPF Macrobatch 3). The tests focused on two areas: alternative frits to Frit 200 and alternative chemical process cell strategies. The tests were conducted in dry-feed, batch furnace designed to measure the relative melt rates. The tests indicated that melt rate is a function of alkali content of the feed or the ratio of nitric acid to formic acid during melter feed preparation of the glass. Higher levels of alkali in the feed and more formic acid corresponded to increased melt rate for this particular system. The testing led to the recommendation for a frit change in the DWPF from Frit 200 to Frit 320 for sludge batch 2. In making the recommendation, a systems approach was used to ensure that melt rate improvements do not lead to other processing problems such as a restrictive operating window.

Test Methods

The melt rate furnace currently utilized is a specially designed top loading furnace. A six inch hole through the top of the furnace allows the crucible to be suspended from the top of the furnace to expose only the bottom of the beaker to the interior. The heat transfer in the crucible is designed to be one-dimensional heating from the bottom. An insulating sleeve holds the 4.5" diameter stainless steel crucible. The crucible is charged with sufficient dried melter feed to produce 500 grams of glass. The initial height of the melter feed is approximately 3" and the final height of glass is approximately 1". All tests were conducted at a constant waste loading of 25% for FY00 tests and 23.2% for FY01 tests.

After charging, the crucible is lowered into the 1150°C furnace. The crucible is either removed after a specified time or when the vapor space reaches a certain temperature. Thermocouples in the batch at various heights monitor the temperature and a boroscope can be used to monitor batch height during the run. Severe bridging limits the ability to determine melt rate from the temperature readings, therefore melt rate determinations were made by measuring the height of glass in the sectioned crucible.

Correlation of Alkali Content and Melt Rate: Alternative Frit Tests

Twelve alternative frit formulations were developed and tested during FY01, along with the current process frit (Frit 200) and a frit developed previously by SRTC (Frit 165). Frit compositions are shown in Table II. All frits were tested with the same batch of sludge to preclude changes in the sludge affecting the frit tests.

Table II. Target Compositions of Frits Tested in the Melt Rate Furnace (Wt% Oxide Basis)

Frit	Al	B	Li	Na	Mg	Si	Other (La, Ti, Zr)
165	-	10.00	7.00	13.00	1.00	68.00	1.00
200	-	12.00	5.00	11.00	2.00	70.00	-
202	-	8.00	7.00	6.00	2.00	77.00	-
303	2.29	20.13	10.12	-	-	67.46	-
304	2.29	6.71	5.80	18.07	-	67.13	-
307	-	12.08	10.74	4.67	-	72.51	-
313	-	6.71	10.74	5.94	-	73.80	-
314	-	20.13	5.94	6.12	-	65.79	2.01
315	-	20.13	10.03	0.00	-	69.84	-
320	-	8.00	8.00	12.00	-	72.00	-
320-A	-	8.00	11.00	9.00	-	72.00	-
322	-	8.00	5.00	10.00	-	77.00	-
323	-	15.00	5.19	8.28	-	71.53	-
324	-	15.00	8.28	5.19	-	71.53	-
325 / 202	-	8.55	7.55	9.10	1.5	72.80	0.5
326	-	8.00	8.00	11.00	1.0	72.00	-

The results of the melt rate tests are shown in Table III. The results were analyzed by the JMP4 statistical program to determine if a correlation existed between alkali content of the frit and the measured melt rate. Although the data set was not ideal, as the data was not designed to fit a statistical sample matrix, the analysis indicated that melt rate was a function of alkali content.

Table III. Melt Rate of Alternative Frits Tested

Frit Designation	Alkali Content (Wt % oxide)	Melt Rate (in/hr)
304	23.9	1.13
320	20.0	1.05
313	19.5	1.01
326	19.0	0.95
165	20.0	0.95
307	15.4	0.93
325 / 202 (50/50 mixture)	16.7	0.87
322	15.0	0.87
324	13.5	0.79
200	16.0	0.75
314	12.1	0.66
323	13.5	0.62
315	10.0	0.62
303	10.1	0.51

Two alkali elements are present in the frits tested, lithium and sodium. Lithium has a much lower molecular weight than sodium, therefore, an equal amount of lithium in the frit by weight represents a higher mole fraction of alkali in the frit than sodium. As shown in Figure 3, a linear curve fit can be applied to the data to predict melt rate from either weight % alkali content or mole % alkali content in the frit for this sludge batch. Runs with high levels of boron in the frit are highlighted on Figure 1 as these runs did not follow the general trend that increasing alkali increases melt rate. These runs are not included in the linear curve fit.

A new frit, Frit 320-A was developed to determine if the melt rate is a function of weight % alkali or mole fraction. The new frit was the same as Frit 320, with the lithium and sodium concentrations varied to increase the mole fraction of alkali in the frit. The results of this test indicate that melt rate corresponds to weight % alkali, but additional tests are required for confirmation.

The melt rate team recommended that DWPF switch from Frit 200 (16 wt% alkali) to Frit 320 (20 wt% alkali) for Macrobatch 3 (MB3) processing. Although Frit 304 had a higher alkali content and melt rate, the models currently used for DWPF processing did not accurately predict the durability of the glass as defined by the Product Consistency Test (PCT). Efforts are currently underway to implement Frit 320 for MB3 and to investigate ways to improve other process models to increase the operational window for DWPF while maintaining both process and product performance integrity.

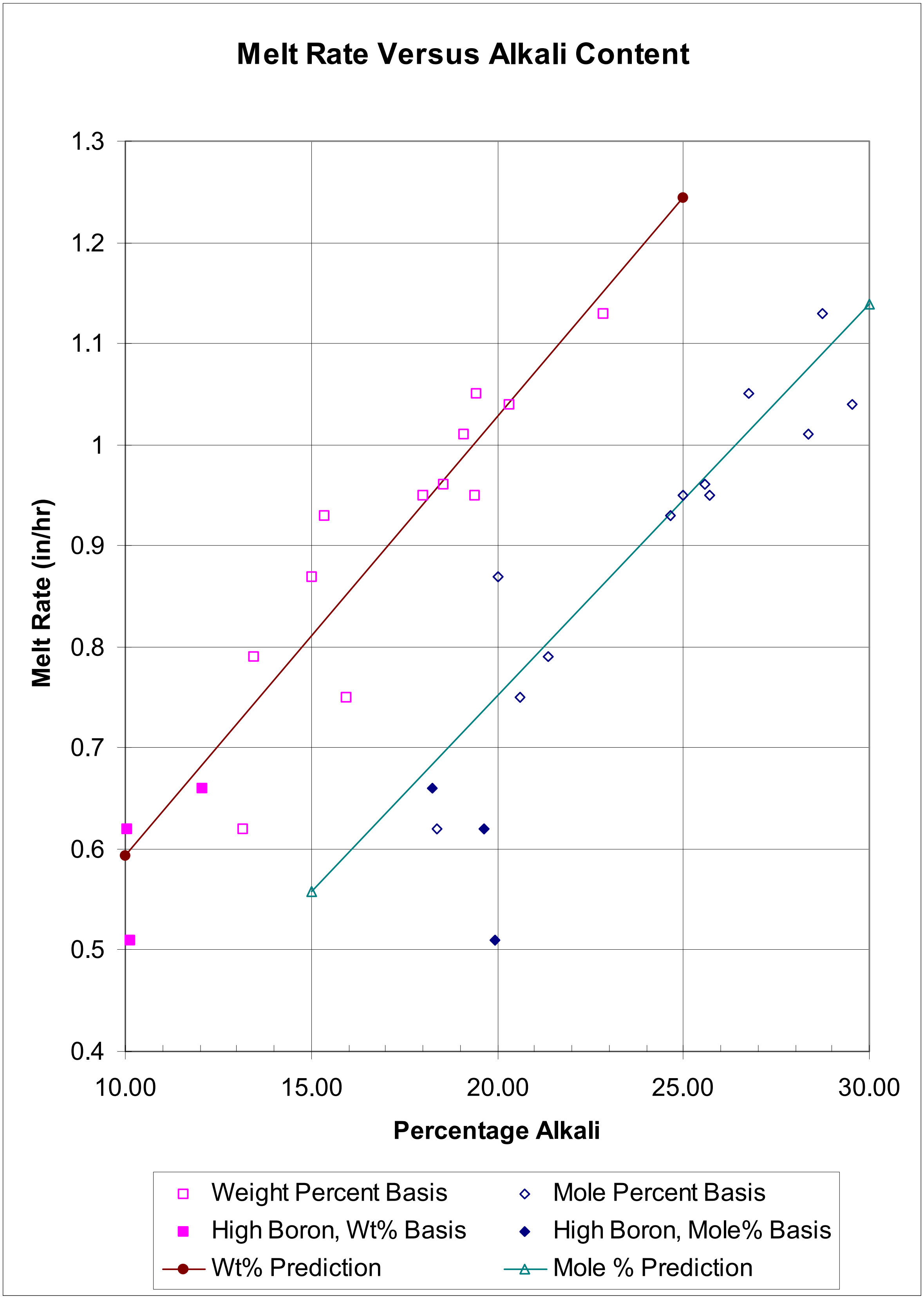


Fig. 3. Melt Rate Versus Alkali Content

Correlation of Alkali Content and Melt Rate: Alternative Washing Tests

In addition to the correlation noted during the alternative frit study, a similar trend was noted between alkali content and melt rate during tests with overwashed and underwashed sludge. The sludge is washed to remove soluble species, such as sulfate, that negatively affect melter operation. Washing the sludge removes sodium compounds, therefore, underwashed sludge has a higher alkali content than nominal feed and overwashed feed has the lowest alkali content (1). The tests in this series were conducted with feed partially dried versus the completely dried feed during alternative frit tests, therefore, the results do not compare directly to the frit tests. However, the melt rate tests indicate that melt rate decreases with increased washing (or increased sodium content), as shown in Table IV.

Table IV. Linear Melt Rate of Underwashed, Nominal Washed, and Overwashed MB3 Sludge

Sludge Type	Melt Rate (in/hr)
Underwashed	0.68
Nominal Wash	0.57
Overwashed	0.47

Correlation of Melt Rate to Nitric Acid / Formic Acid Ratio

Tests were conducted in FY00 and FY01 to determine the impact on melt rate of changes to the ratio of nitric acid and formic acid added during the melter feed process. The redox state of the glass is impacted by the ratio of nitrate to formate in the feed, as nitrate is an oxidizer and formate is a reducing agent. Redox state of the glass product is measured by determining the ratio of reduced iron (Fe^{+2}) to the total amount of iron in the glass. The current target for redox state is a ratio of 0.2 $Fe^{+2}/\Sigma Fe$, as predicted by a process model based on the ratio of nitrate to formate in the melter feed.

Tests were conducted with various ratios of nitric acid to formic acid during the feed preparation process to determine the impact on melt rate. The tests were conducted during FY00 and utilized Macrobatch 2 (MB2) sludge simulant as the tests in FY00 were focused on improving the melt rate of MB2. Sufficient similarity exists between the sludge batch compositions that the results should translate from one sludge batch to another. As shown in Table V, the melt rate of feed with more nitric acid had a significantly lower melt rate than feeds with more formic acid. Two factors may be contributing to the increased melt rate with increased formic acid. Nitrate destruction occurs at high temperature and may be contributing to foaming. Substitution of formic acid would decrease the amount of nitrate and reduce the amount of foaming occurring as a result of nitrate destruction. Secondly, the more reducing nature of melter feed with increased formic acid may lead to less offgas generation from reduction reactions during the melting process. The "blended" test represents the current ratio of formic acid to nitric acid in the DWPF process, therefore the amount of melt rate improvement that could be achieved by increasing the formic acid is limited based on these test results.

Table V. Nitric Acid / Formic Acid Melt Rate Tests (FY00 Testing)

Sludge Type	Melt Rate (in/hr)
Formic Acid Only	0.59
"Blended" 80% Formic Acid / 20% Nitric Acid	0.57
90% Nitric Acid / 10% Formic Acid	0.33

Test Limitations

The melt rate furnace utilized a batch process and the melter feed was dried before testing while DWPF utilizes a slurry-fed continuous process. Direct translation of the results from the melt rate furnace to DWPF is not possible but it is assumed that trends would be. SRTC has developed a slurry-fed continuous melt rate furnace as well as a prototypical joule-fired mini-melter to fill the gap between the dry-batch tests and the DWPF. Tests will be conducted in these tools during FY02 to verify that the trends and correlations noted during the FY00 and FY01 melt rate testing are the same during slurry-feeding.

REFERENCES

1. "Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms", EM-WAPS Rev 2, DOE/EM-0093, December 1996.

2. D. P. LAMBERT, T. H. LORIER, D.K. PEELER, and M. E. STONE, "Melt Rate Improvement for DWPF MB3: Summary and Recommendations," WSRC-TR-2001-00148, Savannah River Site (2001).

3. M. E. STONE and D. P. LAMBERT, "DWPF Macrobatch 2 Melt Rate Tests," WSRC-TR-2000-0395, Savannah River Site (2000).