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November 29, 2004

Waste Management Symposium
Tucson, AZ, United States
February 27, 2005 through March 3, 2005

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JOULE-HEATED CERAMIC-LINED MELTER TO VITRIFY LIQUID RADIOACTIVE WASTES CONTAINING AM241 GENERATED FROM MOX FUEL FABRICATION IN RUSSIA

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ABSTRACT

The governments of the United States of America and the Russian Federation (RF) signed an Agreement September 1, 2000 to dispose of weapons plutonium that has been designated as no longer required for defense purposes. The Agreement declares that each country will disposition 34MT of excess weapons grade plutonium from their stockpiles. The preferred disposition technology is the fabrication of mixed oxide (MOx) fuel for use or burning in pressurized water reactors to destroy the plutonium. Implementation of this Agreement will require the conversion of plutonium metal to oxide and the fabrication of MOx fuel within the Russian Federation. The MOx fuel fabrication and metal to oxide conversion processes will generate solid and liquid radioactive wastes containing trace amounts of plutonium, neptunium, americium, and uranium requiring treatment, storage, and disposal.

Unique to the Russian MOx fuel fabrication facility's flow-sheet is a liquid waste stream with high concentrations (~1 g/l) of ²⁴¹Am and non radioactive silver. The silver is used to dissolve PuO₂ feed materials to the MOx fabrication facility. Technical solutions are needed to treat and solidify this liquid waste stream. Alternative treatment technologies for this liquid waste stream are being evaluated by a Russian engineering team. The technologies being evaluated include borosilicate and phosphate vitrification alternatives. The evaluations are being performed at a conceptual design level of detail under a Lawrence Livermore National Laboratory (LLNL) contract with the Russian organization TVEL using DOE NA-26 funding. As part of this contract, the RF team is evaluating the technical and economic feasibility of the US borosilicate glass vitrification technology based on a Duratek melter to solidify this waste stream into a form acceptable for storage and geologic disposal.

The composition of the glass formed from treating the waste is dictated by the concentration of silver and americium it contains. Silver is widely used as an additive in glass making. However, its solubility is known to be limited in borosilicate glasses. Further, silver, which is present as a nitrate salt in the waste, can be easily reduced to molten silver in the melting process. Molten silver, if formed, would be difficult to reintroduce into the glass matrix and could pose operating difficulties for the glass melter. This will place a limitation on the waste loading of the melter feed material to prevent the separation of silver from the waste within the melter. If the silver were recovered in the MOx fabrication process, which is currently under consideration, the composition of the glass would likely be limited only by the thermal heat load from the incorporated ²⁴¹Am. The resulting mass of glass used to encapsulate the waste could then be reduced by a factor of approximately three.

The vitrification process used to treat the waste stream is proposed to center on a joule-heated ceramic lined slurry fed melter. Glass furnaces of this type are used in the United States to treat high-level waste (HLW) at the: Defense Waste Processing Facility, West Valley Demonstration Project, and to process the Hanford tank waste. The waste will initially be blended with glass-forming chemicals, which are primarily sand and boric acid. The resulting slurry is pumped to the melter for conversion to glass. The melter is a ceramic lined metal box that contains a molten glass pool heated by passing electric current through the glass. Molten glass from the melter is poured into canisters to cool and solidify. They are then sealed and decontaminated to form the final waste disposal package. Emissions generated in the melter from the vitrification process are treated by an off-gas system to remove radioactive contamination and destroy nitrogen oxides (NO_x).

INTRODUCTION

The United States and the Soviet Union accumulated large stockpiles of weapons-grade plutonium throughout the Cold War, which are no longer necessary today for nuclear weapons. In 1995, US President Bill Clinton announced that the United States possessed over 50t of plutonium in excess of national security needs. RF President Boris Yeltsin reciprocated by announcing in 1997 that Russia intended to remove 50t of plutonium from its defense programs.

On September 1, 2000, US Vice President Al Gore and Russian Prime Minister Mikhail Kasyanov officially signed the US-Russia Plutonium Disposition Agreement (1). According to the agreement, both countries must dispose of 34t of weapons-grade plutonium. Russia intends to burn all 34t as MO_x fuel. Both the United States and the Russian Federation must design and construct MO_x fuel fabrication plants in order to dispose of the excess plutonium. The two countries are mutually cooperating to design nearly identical MO_x fuel fabrication plants for construction at the Tomsk site in the RF and at the Savannah River Site in the United States.

Fabrication of MO_x fuel will dissolve the plutonium using silver to speed the reaction. The plutonium in the RF also contains higher levels of ²⁴¹Am than in the United States. This ²⁴¹Am is a byproduct of plutonium decay and must be removed prior to fabricating the MO_x fuel. The result of these two steps is a nitric acid waste stream containing significant fractions of silver and americium (Table I) that will require treatment prior to disposal. The US MO_x fabrication plant will treat this waste through cementation and send it to the Waste Isolation Pilot Plant (WIPP) in New Mexico. However, the high concentration of ²⁴¹Am within the RF waste makes this an unacceptable alternative since the solids waste must be stored for decades until a geologic disposal facility is available in the RF. One of the options being considered for treatment of the ²⁴¹Am waste is to convert it to a borosilicate glass. This paper describes the glass chemistry and plant design concept that could be used for vitrifying the waste.

Table I Americium Waste Stream Parameters

Parameter	Expected (annual)
Generated volume	11,270 L
²⁴¹ Am	29.5 kg
²⁴¹ Am alpha activity	3,750 TBq
Plutonium	< 205 g
[H ⁺]	9.4 N

Parameter	Expected (annual)
Uranium	< 143 g
Gallium	Trace
Silver	~ 142 kg
Zirconium	~ 40 kg
Aluminum	~ 1 kg
Trace Metals	Pb, Tl & Hg
Chloride content	< 1 µg/L
Total nitrates salts	< 250 kg
Organics (TBP) content	< 300 mg/L

GLASS CHEMISTRY

Duratek and Vitreous State Laboratory (VSL) have provided support to the RF MOx fuel waste treatment effort by performing analyses and evaluations of the vitrification option and have developed initial process concepts and designs. A major aspect of that evaluation involves the sizing of the vitrification facility. The facility size is determined not only by the waste stream generation rate and desired treatment rate but also by the expected waste loadings of the americium stream in the glass product. In the present work, the principal waste loading limiting factors have been evaluated, various process alternatives have been investigated, and potential glass formulations have been identified.

Present projections show an estimated annual generation rate for the RF americium stream corresponding to 450 – 550 kg of total waste oxides. On an oxide basis, the major constituents are projected to be silver (60 - 70 wt%), which is used in the dissolution process, gallium (~ 14 wt%), which is used as a phase-stabilizer, and americium (7 – 21 wt%). As a result, the waste loading in the glass is likely to be determined by the achievable silver loading and the allowable decay heat in the vitrified product. Duratek and VSL have investigated the interplay between these factors for a variety of possible processing scenarios.

A limit on the allowable decay heat in the vitrified product has not yet been determined for the RF facility. The limit for the vitrified product from typical European reprocessing facilities is 4750 W per metric ton; for comparison, the limit for US vitrified HLW is about one-sixth of this. Assuming the European limit, decay heat would limit the americium content to about 4 wt% AmO₂, which would correspond to waste oxide loadings of about 20 – 60 wt%. At these waste loadings, the silver content would be about 12 - 40 wt% Ag₂O. Such high silver loadings are unrealistic for viable waste glasses. As a result, silver management is the more limiting factor and the primary determinant of the facility size and total quantity of glass produced.

Clearly, if silver is not incorporated into the glass product, waste loadings could be increased towards the decay heat limit. There are many possibilities for wet chemical processes for silver removal, including various redox reactions, as well as precipitation, ion exchange, and electrochemical processes. Indeed, in the French MOx process, silver is recovered from this stream and recycled for reuse. However, this adds further process complexity to the management of a very small waste stream, which may not be desirable in the present application.

Silver displays a wide range of solubilities in glass melts. The solubility is highly dependent on the glass composition, temperature, and redox state. Silver is very easily reduced to the metallic state, which can present processing problems unless the melting system is designed to accommodate a molten metal phase. Even under globally oxidizing conditions, transient reducing conditions, (e.g., in the cold cap) can result in metal production; once formed, the metal rapidly segregates from the melt by density and is very slow to re-oxidize. In silicate melts, silver solubility is generally low. There are no naturally-occurring silver silicates but synthetic feldspars and zeolites have been reported. Although simple borate systems with up to 30% Ag₂O have been reported, these are not likely to provide viable waste glasses. Phosphate melts can incorporate relatively large amounts of silver but have many undesirable corrosive features in terms of waste vitrification; they also tend to be relatively reducing. In the present work, we have developed viable non-phosphate waste glasses that incorporate 1.1 – 1.7 wt% Ag₂O with no metal formation. These glasses have been subjected to structural characterization by Raman spectroscopy and X-ray absorption spectroscopy (EXAFS, XANES). There is evidence that the ability to incorporate silver without metal formation is quite sensitive to the prevailing glass structure, which provides a guide for further increasing the levels achievable in viable waste glasses. These silver loadings have been used to provide a sizing basis for vitrification facilities with and without the use of silver removal.

PLANT DESIGN

The concentration of silver within the waste is the controlling parameter in designing a plant to treat the waste through vitrification. With the concentration of silver listed in Table I, the amount of waste contained in the glass (i.e., waste loading) will be limited to approximately 3.7 percent to prevent the separation of the silver from the glass within the melter. The remainder of the glass will be composed of glass forming chemicals. If, however, the concentration of silver in the waste could be lowered or even eliminated, the waste loading of the glass would only be limited by the internal radio-decay heat generation. This would allow the waste loading to increase by a factor of more than three.

The waste loading of the glass plays a critical factor in determining the size of plant components, which in turn dictates the cost of treating the waste. This is best demonstrated using the melter as an example. If the specific glass production rate of the melter is 500 kg-glass/m²/day, the size of the melter is then easily determined from the desired waste processing rate, the plant availability and waste loading using equation 1.

$$S_{Melter} = \frac{M_{Waste}}{T \times W \times A} \quad (\text{Eq. 1})$$

Where:

S = melter glass pool surface area (m²)

M = waste processing rate (kg/day)

W = Glass waste loading (fraction)

A = plant availability (fraction)

T = specific melter glass production rate (kg/m²/day)

From this equation, it is obvious that the size of the melter is inversely proportional to the waste loading of the glass. Removal of silver from the waste would allow a many fold increase in the waste loading and a resulting decrease in the size of the melter. The reduction in the melter size

would also lead to corresponding reductions in the size of all plant components as shown in Table II. The reduction in the size of plant equipment would drastically alter the cost of the treatment facility.

TABLE II Melter Size Comparison for Silver Removal

Parameter	Silver Present	Silver Removed
Silver content of waste (wt%)	0.97	~0
Melter surface area (m ²)	0.11	0.02 ¹
Mass of glass produced yearly (kg)	25,450	7,890
Feed tank volume (L)	1700	530
Melter emission rate (m ³ /s)	0.0465	0.0145

¹The specific melter glass production rate increases with reduced melter size

The plan for the MOx fabrication plant is not currently planning to remove silver from the waste.

VITRIFICATION PROCESS

Waste will be received from the MOx fuel fabrication plant as a concentrated nitric acid stream with the previously discussed composition. The waste will be collected from the fuel fabrication plant in the waste receipt tank (WRT) located in the vitrification facility (Figure 1). It will then be batch transferred to the melter feed preparation tank (MFPT) for preparation of melter feed batches (Figure 2). Process solutions recycled from the off-gas system will be added to the MFPT for treatment in the melter. Water will also be added to the feed during feed preparation to provide sufficient liquid volume to suspend the required glass forming chemicals (GFCs). The GFCs, which are composed primarily of sand, will then be added to the MFPT and thoroughly mixed to form a melter feed slurry. This slurry will then be batch transferred to the melter feed tank (MFT). The feed slurry will be continuously pumped to the melter at a controlled rate to convert it to glass.

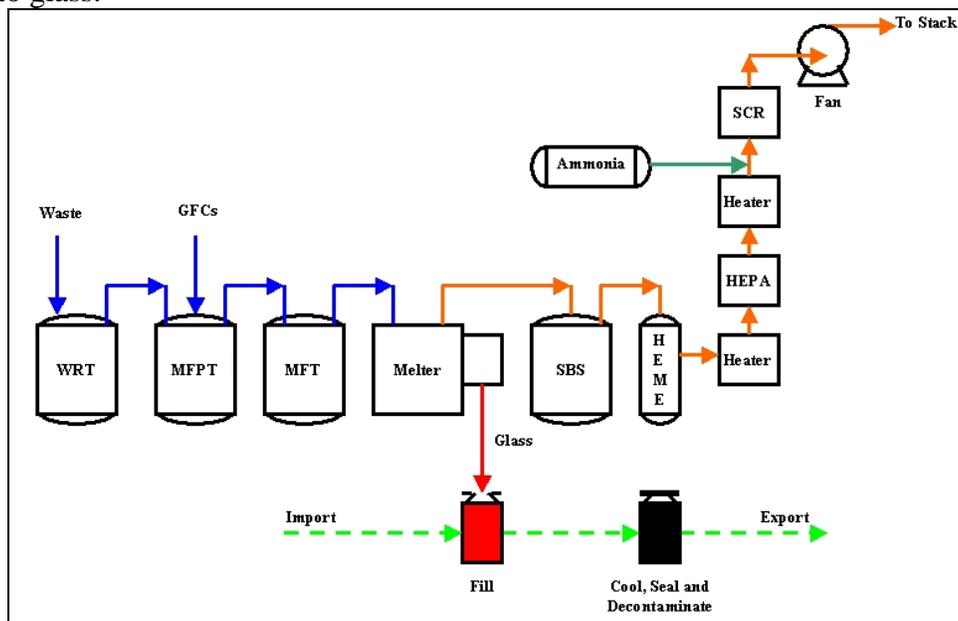


Figure 1 Simplified Vitrification Process Block Diagram

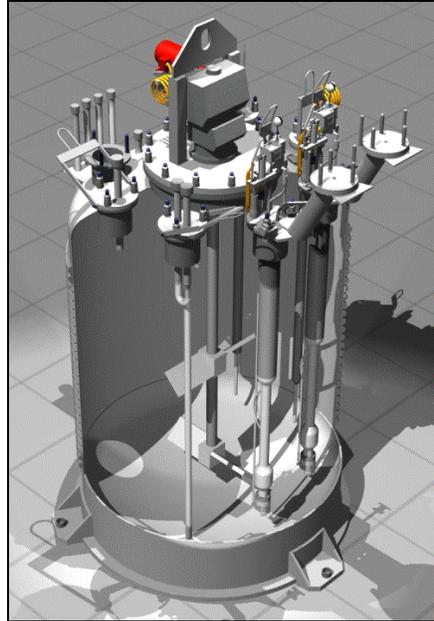


Figure 2 Typical Melter Feed Tank (1.2-m diameter) Section View

The melter will be a joule-heated ceramic-lined slurry-fed glass furnace (Figure 3). Feed slurry from the MFT will be added to the melter through feed nozzles located in the lid of the melter. The total feed rate will be approximately 7.5 liter per hour. The feed slurry will fall from the feed tube through the melter gas space onto the surface of the glass pool. The feed materials will form a layer of reacting feed slurry on the surface of the glass pool referred to as the cold cap. As the cold cap is heated by heat transfer from the glass pool, volatile components within the feed will evolve to the off-gas system while the remaining components melt into the glass pool.

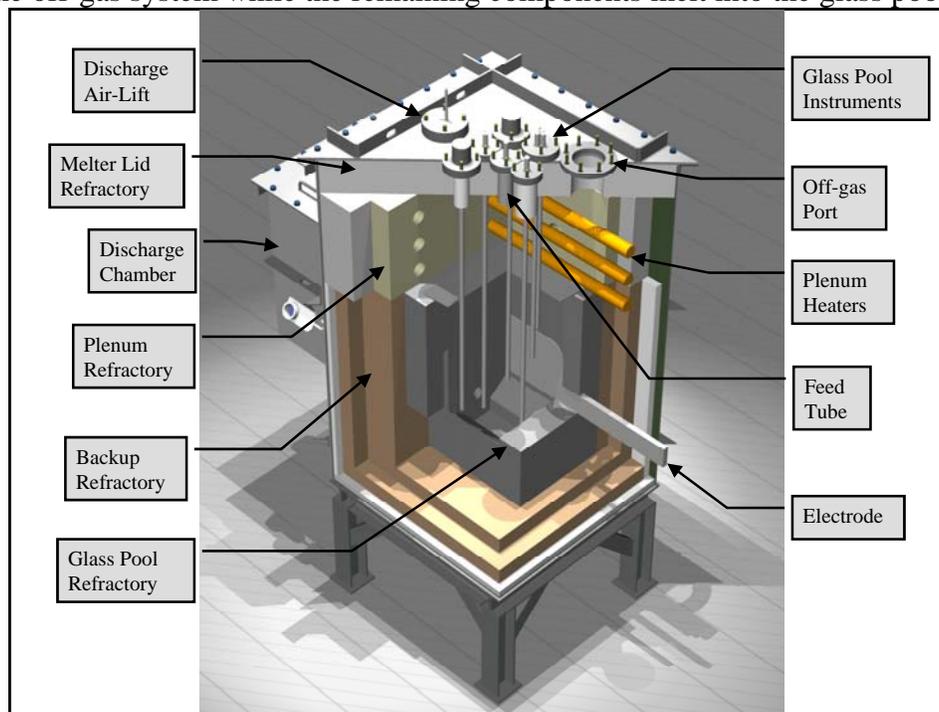


Figure 3 Waste Glass Melter (1.2-m wide by 1.2-m long) Section View

The melter will have a glass pool surface area of 0.11 square meters and will produce glass at approximately 100 kg of glass per day. The heat needed to convert the waste feed slurry to glass will be transferred from submerged metallic electrodes to a molten glass pool. The glass will be actively mixed using a proprietary air sparging system to enhance the waste-processing rate, which reduces the melter size.

The primary design concern for the melter will be the high concentrations of silver within the feed. The design approach for the waste treatment process will be to avoid the formation of elemental silver within the melter. However, the melter must be designed to accept silver should it form. If elemental silver forms within the melter, it will have a much higher density than the glass (10,500 versus 2400 kg/m³) and will sink to the floor of the melter. There the molten silver (melting point 962°C) will form a highly conductive layer and may seep into gaps within the refractory. The highly conductive silver layer would tend to preferentially draw the electrical current flowing through the glass in a similar manner to noble metals sludge in high-level waste glass melters. The current flowing through the silver layer would not contribute to the heating of the bulk glass but would contribute to heating of the electrode. The design of the melter must therefore allow for continued operation with the silver layer such that the current passing through the electrodes does not rise sufficiently to damage them.

The design features that will minimize the increase in electrode current passage are nearly identical to those currently being employed in the melter to process high-level waste at the Hanford site by the Department of Energy. The key feature will be to maximize the vertical separation between the silver layer and the electrodes. Without the planned active glass pool agitation, the floor of the melter would become cold enough to allow crystal growth within the stagnant glass. However, the use of an active glass pool agitation system will maintain uniform glass pool temperature and prevent localized glass overheating or cooling.

The continuous addition of feed will form glass, which raises the level of glass within the melter. Periodic discharges of glass from the melter into canisters will be performed to maintain the glass level with a control band. Glass will be discharged from the melter via an airlift system contained within one wall of the melter refractory. The glass from the airlift will flow down a trough contained in a heated discharge chamber and fall into the awaiting canister. The canister will be sealed to the melter by a pour spout assembly that is suspended from the bottom of the discharge chamber. The pour spout will prevent unrestricted airflow into the discharge chamber while the canister is in place. It will also compensate for potential out-of-position tolerances of the canister. The pour spout will contain a method for viewing the glass pour stream during pouring operations.

The canisters will be positioned under the pour spout by a four-position turntable. The turntable will allow for canister cooling, filling, loading, and un-loading to occur in parallel. Filled canisters will be removed from the turntable and are then sealed and decontaminated prior to placing them into storage.

The melter will generate toxic and radioactive emissions during the glass making process. The melter exhaust gas must be contained and treated to protect the environment and plant personnel. To prevent the release of materials from the system, the melter off-gas system and feed system

will be maintained under a vacuum by the off-gas system. The emissions from the process will be treated in the off-gas system prior to release to the atmosphere. The total expected melter emissions rate is 0.0465 cubic meters per second at 500 degrees centigrade.

The exhaust gas from the melter will be conditioned by a film cooler. The film cooler will be the first component of the off-gas system and will be installed into the lid of the melter to prevent the deposition of entrained feed solids at the entrance to the off-gas system. The film cooler prevents solids buildup by injecting air to cool the melter exhaust gas into a temperature range that has been shown to reduce the rate of deposit of material and the adherence of any deposits to the walls of the off-gas duct. The film cooler will consist of a series of louvers positioned along its circumference. Air will be injected through these louvers to form a film of air along the ducting wall to prevent the deposition of solids. As this film naturally breaks down due to turbulence, the injection air will mix with the off-gas cooling it. Air will be injected into the melter exhaust down-stream of the film cooler for melter vacuum control, which will complete the cooling of the gas to the desired temperature.

The submerged bed scrubber (SBS) will cool the off-gas to the desired temperature by passing the gas through a water flooded packed bed. The off-gas will enter the SBS through a pipe that will direct the gas to the bottom of the packed bed. As the off-gas rises through the bed, it will be cooled and a significant portion of the entrained solids will be removed (Figure 4). The packing in the bed serves to breakup the gas bubbles to promote better contact between the gas and SBS water. The amount of condensation of steam exhausted from the melter will be controlled through control of the amount of cooling of the SBS liquid. Water condensed in the SBS bed will be collected in a tank that surrounds the bed. This liquid, which will contain appreciable quantities of radioactive materials, will be periodically transferred to the MFPT for recycle into the melter feed. To aid in the removal of any solids, the SBS will also contain a solids removal system.

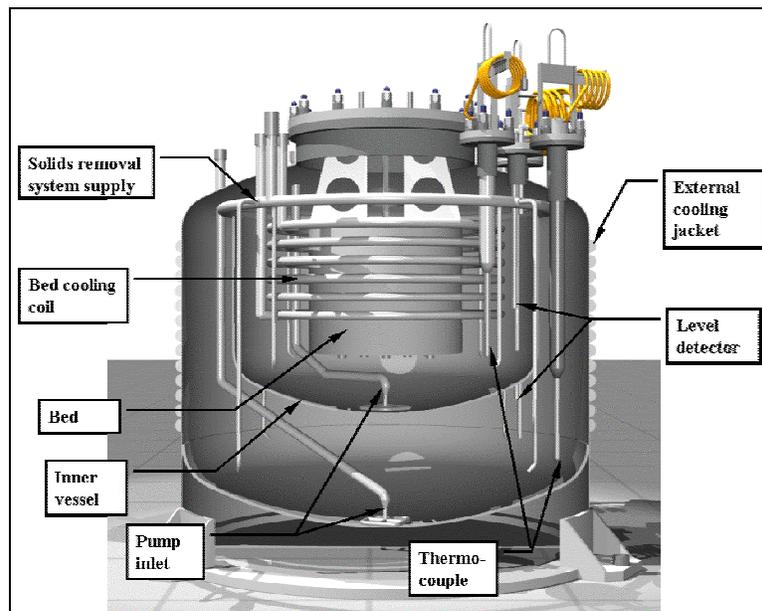


Figure 4 SBS (1.2-m diameter) Section View

The cooled gas that exits from the SBS will then enter the high efficiency mist eliminator (HEME). The HEME is essentially a wet filter that will remove entrained water droplets and

mists from the gas stream at element surface velocities of less than 12 meters per minute. The HEME will consist of a tank containing a filter element on a support grid. The HEME will be designed to allow the filter element to be routinely sprayed with clean water to remove the buildup of any solids that may occur. Water collected or sprayed on the HEME will drain back to the SBS tank. Gases exiting the HEME will be heated to lower their relative humidity and passed through high efficiency particulate air (HEPA) filters to prevent the release of radioactive contamination.

The final step in the off-gas treatment system will destroy the nitrogen oxides (NO_x) produced within the melter from the decomposition of feed nitric acid. A selective catalytic reduction (SCR) unit has been selected to treat the NO_x. This unit will convert the nitrogen oxides to nitrogen and water by reacting it with ammonia in the presence of a catalyst at elevated temperatures.

The plant process equipment will be located within three separate contamination control areas for ease of maintenance and to prevent the spread of contamination. Separate plant equipment areas will be provided for the feed vessels, melter equipment, and off-gas equipment.

The feed vessel area will contain the three vessels of the melter feed system. The frequency of routine maintenance for this system is much less than some other systems. Maintenance activities will be limited to the replacement of failed components. The melter area will contain the melter, pour spout, canister glass level detection system and canister filling station. As with the feed system area, the maintenance of the melter will be limited to replacing failed components. Most activities can be performed by hand with limited personnel exposure since the melter refractory and shell provide substantial shielding. Additional shielding may be required in the area containing the glass filled canisters. The off-gas area will contain the portions of the off-gas system that will collect appreciable amounts of the radionuclides contained in the waste.

CONCLUSIONS

An americium waste stream containing a substantial amount of silver is to be generated during the MO_x fuel fabrication process in the RF. One option for treating this waste is through borosilicate glass vitrification within a traditional joule heated ceramic lined slurry fed melter. The size of the melter and facility will be dictated by the concentration of silver in the waste. Glasses can be formulated with silver concentrations of 1.1-1.7 wt% silver with the possibility of higher waste loadings indicated in test results. The plant required to continuously process the silver containing waste stream has been defined and is relatively small in size. The feed system will fit within an envelope of 2-m wide, 5-m long and 3-m high. The melter and off-gas systems will require even less space. If, however, the silver can be removed and recycled prior to vitrification, the size of the melter and plant could be dramatically reduced with a corresponding reduction in the facility cost and would easily fit within a single glove-box.

REFERENCES

1. Agreement Between The Government Of The United States Of America And The Government Of The Russian Federation Concerning The Management And Disposition Of Plutonium Designated As No Longer Required For Defense Purposes And Related Cooperation, September 2000.