

## **Control of the Reduction/Oxidation State of the High Level Waste Form in the Defense Waste Processing Facility at the Savannah River Site - 12451**

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### **ABSTRACT**

The Defense Waste Processing Facility at the Savannah River Site treats and immobilizes High Level Waste into a durable borosilicate glass for safe, permanent storage. Among the parameters important to the overall process is the reduction/oxidation state of the glass. Control strategies for the reduction/oxidation state of the glass have been developed and evolved over the last 20 years to provide a current strategy which is both accurate and robust. A description of the methodologies implemented to control, evaluate, and validate the reduction/oxidation state of the glass is discussed along with the impact of future facility changes (made to pursue a more aggressive program to empty High Level Waste tanks at the Savannah River Site) on the reduction/oxidation state of glass.

### **INTRODUCTION**

Generically, final processing of High Level Waste generated from the production of nuclear material at the Savannah River Site since the 1950s (approximately 136 million liters) occurs at the Defense Waste Processing Facility by first treating the waste via a complex sequence of controlled chemical reactions, followed by blending the treated waste with glass formers. The blended waste is then vitrified into a borosilicate glass form, and the resulting molten glass poured into stainless steel canisters. The current DWPF flowsheet is shown in Figure 1.

Nominally, 22,500 liters of sludge is received on a batch-by-batch basis in the Sludge Receipt and Adjustment Tank (SRAT) from a 3.7 million liter feed tank. The sludge is chemically adjusted in the SRAT via addition of concentrated nitric and formic acids. The purpose of the chemical adjustment is to acidify the incoming sludge to adjust the rheological properties to improve processing, remove mercury from the sludge feed, and to prepare the sludge feed for melter operation by controlling the reduction/oxidation state of the glass. With respect to the reduction/oxidation state of the glass, the important parameter is the ratio of nitric and formic acid added. The SRAT also receives and processes by-products from salt processing, namely an actinide-rich stream containing primarily monosodium titanate solids as well as a cesium-rich dilute nitric stream. Each of these streams has the potential to impact the reduction/oxidation state of the glass, and must be accounted for during acid addition in the SRAT. Following chemical adjustment and concentration in the SRAT, the sludge material is transferred to the Slurry Mix Evaporator (SME) where the material is blended with frit (glass former). The SME represents a hold point in the process to ensure the contents will produce acceptable glass (based on statistical process control rather than statistical quality control). In addition to glass acceptability, the reduction/oxidation state of the glass is evaluated prior to being fed to the

melter. If the blended SME material is deemed acceptable, the material is transferred to the Melter Feed Tank (MFT). The MFT represents a transition in the process from a batch to continuous process, as the MFT continuously feeds the melter. During normal operation, the melter constantly receives a small stream of slurry from the MFT (nominally 3.8 liters per minute) and melts the feed through the use of an electric current which is passed through the melt pool by two sets of electrodes, resulting in heat-up of the melter feed (i.e. Joule heating). Molten glass from the melt pool is then transferred into stainless steel canisters for permanent immobilization.

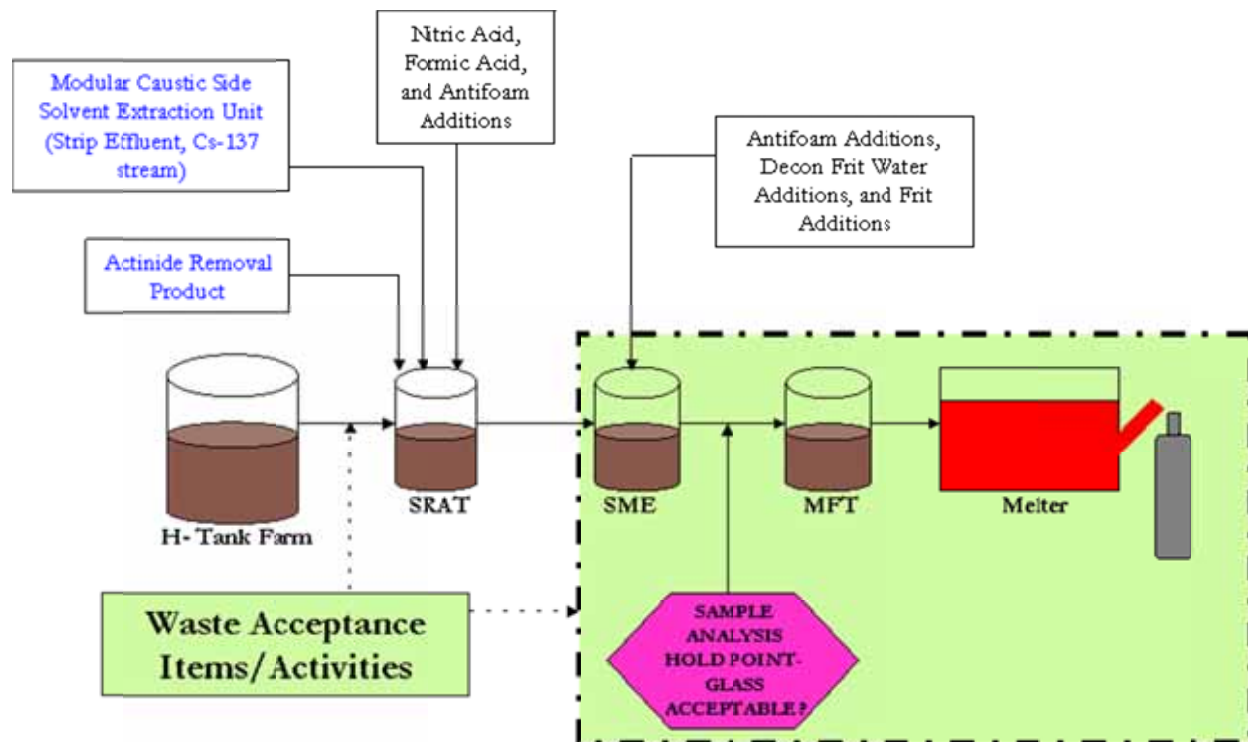


Fig. 1. Schematic providing an overview of the current Defense Waste Processing Facility flowsheet.

Savannah River Remediation (SRR) LLC is currently pursuing an aggressive program to empty its High Level Waste (HLW) tanks at the Savannah River Site (SRS). To accommodate this program, downstream processes such as the Defense Waste Processing Facility must improve overall throughput. Efforts to improve the overall throughput of DWPF include fundamental changes to the flowsheet depicted in Figure 1. Each of these changes has the potential to change assumptions associated with the control, evaluation, and validation reduction/oxidation state of the glass.

## DISCUSSION

### Basis for Controlling the Reduction/Oxidation State of the Glass

Controlling the reduction/oxidation state of glass is important for melter operation. Melter feed which is too oxidizing can result in excessive melter foaming potentially impacting glass production rates [1]. The reduced production rate with oxidized feeds is due, in part, to reduced heat transfer through the foamy layer formed from excess NO<sub>x</sub> produced from nitrate decomposition and excess oxygen from the deoxygenation of MnO<sub>2</sub> [2,3]. These reactions, combined with the high surface tension of the molten glass, are the primary cause of melter foaming. Uncontrolled melter foaming can cause several significant secondary problems, such as blockage of critical melter off-gas components and inadvertent glass pouring. Tests have shown that foaming is mitigated when reducing agents, such as formic acid, are added to the melter feed stream. A reduced glass contains less dissolved oxygen and should therefore have a lower potential for foaming.

On the other hand, melter feed which is too reducing can result in precipitation of transitional metallic species, potentially leading to melter failure from electrical fault by shorting out electrical pathways in the melt pool. Specifically, in an excessively reducing environment, copper, nickel, and noble metals (such as ruthenium) have a tendency to precipitate out of solution in the melter [2,3]. In addition, reduction of sulfate to sulfide can occur, resulting in the potential for forming metal sulfides with nickel or iron. When transitional metallic species precipitate out of the melt pool, they fall to the bottom of the melter where they provide an alternate current path for the electrodes. This would severely reduce the ability to maintain the bottom of the melt pool at 1150°C, potentially resulting in de-vitrification of the melt pool.

### Defining the Reduction/Oxidation State of the Glass

The reduction/oxidation state of the glass is defined as the ratio of the concentration of iron (II) to total iron ( $Fe^{2+} + Fe^{3+}$ ) in the feed stream.

$$0.0 < \left( \frac{Fe^{2+}}{Fe^{2+} + Fe^{3+}} \right) < 1.0 \quad (\text{Eq. 1})$$

Note that iron (III) is in a higher oxidized state than iron (II). Thus, if the reduction/oxidation ratio in the melter feed is 0.1, the implication is that about 10% of the iron in the melter feed will be in its reduced state ( $Fe^{2+}$ ), while 90% of the iron will be in its oxidized state ( $Fe^{3+}$ ). As more oxidizing agents are added to the feed, the concentration of  $Fe^{3+}$  increases while the concentration of  $Fe^{2+}$  decreases, making the ratio described by Equation 1 smaller. Based on observations of the impact of the glass reduction/oxidation state on melter processing, an acceptable range has been established based upon the measured  $Fe^{2+}/(Fe^{2+} + Fe^{3+})$  ratio. The established range was determined to be greater than or equal to 0.09 (to prevent foaming via the deoxygenation of manganese species) and less than or equal to 0.33 (to prevent metallic nickel and nickel sulfide formation).

As a result of the potential impacts of introducing overly reduced or oxidized feeds to the melter, the reduction/oxidation state of the glass must carefully be controlled within the relatively small operating window described by Equation 2.

$$0.09 < \left( \frac{Fe^{2+}}{Fe^{2+} + Fe^{3+}} \right) < 0.33 \quad (\text{Eq. 2})$$

To ensure melter feed chemistry is adjusted to optimize melter performance, waste processing requires that both an oxidizing acid and a reducing acid be added in the proper balance such that the feed is not overly reducing or overly oxidizing (i.e.  $0.09 < Fe^{2+}/\Sigma Fe < 0.33$ ).

### Controlling the Reduction/Oxidation State of the Glass

As mentioned previously, control of the reduction/oxidation state of the glass is currently achieved through the addition of concentrated nitric acid (oxidizing agent) and formic acid (reducing agent) upstream of the melter. During the first four years of DWPF operation (1996-2000), nitric acid was added in excess of that required for waste processing to assure nitrite destruction was achieved during SRAT processing, thus resulting in a feed which was overly oxidizing. In January 2000, the DWPF implemented a more reducing flowsheet in an effort to control the reduction/oxidation state of the glass and avoid foaming. The aim of the more reducing flowsheet was to target a ratio of  $Fe^{2+}$  to total iron of 0.20. This target has been the historical operating mode for processing waste since 2000.

The primary input determining the relative amounts of acid to be added during the SRAT cycle are derived from a sample analysis obtained shortly following receipt of sludge from the Tank Farm. Since one of the primary objectives of acid addition during the SRAT cycle is to ensure an appropriate reduction/oxidation state of the glass made downstream in the melter, assumptions must be made relative to processes which will occur following the addition of acid. For example, additions of strip effluent (by-product from salt processing), which is a dilute nitric acid stream, are made following acid addition, and can affect the reduction/oxidation state of the final product if not accounted for.

To understand the relationship of the relative amounts of acid added on the reduction/oxidation state of the final waste form, correlations were made between the reduction/oxidation state of the glass and the feed reductant and oxidizer concentrations, which can be easily measured during various phases of processing. Initially, a simplistic model was developed based upon the observation that the concentrations of formate and nitrate appeared to have the largest impact on the reduction/oxidation state of the glass. Crucible testing of melter feed slurries containing varying concentrations of formate and nitrate were evaluated for reduced (i.e.  $Fe^{2+}$ ) and total iron from which the reduction/oxidation ratio was computed. Relationships were developed and refined until, in 1997, the “[F]-[N]” model was established as shown in Equation 3 [4], where [F] and [N] are the concentrations of formate and nitrate (in mol/kg feed), respectively.

$$Fe^{2+}/\Sigma Fe = -0.0257 + 0.31667\{[F] - [N]\} \quad (\text{Eq. 3})$$

However, as evident from the compilation of data from multiple studies (shown in Figure 2), there was significant scatter among the data and the {[F]-[N]} model. In addition, this particular model artificially set the relative reduction/oxidation potentials of nitrate and formate to be equivalent when it was well known that nitric acid is a strong oxidizer and formic acid is a weak reductant. Thus, the data was screened in an attempt to refine the correlation. The resultant “[F]-3[N]” relationship was developed and is shown as Equation 4.

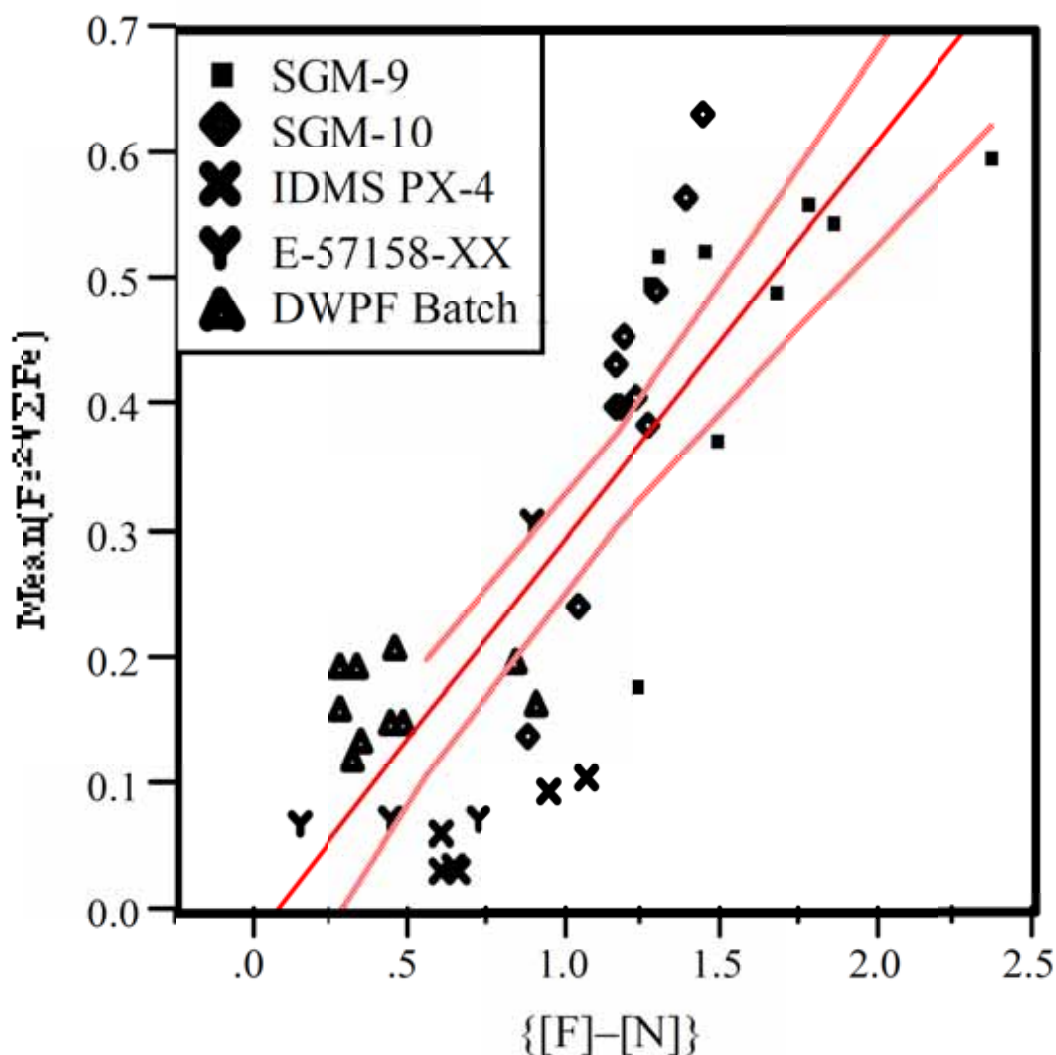


Fig. 2. Relationship between the reduction/oxidation ratio (i.e.  $Fe^{2+}/\Sigma Fe$ ) and the difference between the molar formate and nitrate concentrations plotted from various experimental studies. The label on the ordinate is “Mean ( $Fe^{2+}/\Sigma Fe$ )”.

$$Fe^{2+}/\Sigma Fe = 0.217 + 0.253[F] - 0.739[N] \quad (\text{Eq. 4})$$

Each of the relationships described by Equations 3 and 4 account for feeds in which the primary reductant and oxidant is formate and nitrate, respectively. In 2003, sludge batch planning indicated that future sludge feeds may contain reductants and oxidants in addition to those previously incorporated into correlations. For example, coal and oxalate (reductants) were determined to be prevalent in Tank 7 and manganese (oxidant) was determined to be in relatively high concentrations in Tank 11, each of which was a source tank for upcoming sludge feed to the DWPF. The addition of these constituents required a mechanistic reduction/oxidation model that could account for all oxidizers (nitrate, nitrite, soluble and insoluble manganic species) and reductants (formate, coal, oxalate). In addition, similar to the “{[F]-3[N]}” model, the new model needed to be able to account for the relative oxidizing and reducing power of each

species. To meet these needs, an Electron Equivalents model [5] was developed based on the reduction/oxidation reactions that were known to occur in the melter cold cap [6]. Based upon these reduction/oxidation equilibrium reactions, and the relative number of electrons exchanged during these reactions, the effectiveness of the reductants and oxidants relative to one another can be evaluated. From these relationships, the following model was derived,

$$Fe^{2+} / \sum Fe = 0.2358 + 0.1999 \xi \quad (\text{Eq. 5})$$

$$\xi = (2[F] + 4[C] + 4[O] - 5[N] - 5[Mn]) \frac{45}{T} \quad (\text{Eq. 6})$$

where formate (F), coal (C), oxalate (O), nitrate and nitrite (N), and manganese (Mn) have all been accounted for. All concentrations are given in mol/kg feed, and the signs for the oxidation of the reductants are positive while the signs for reduction of the oxidants are negative indicating gain and loss of electrons, respectively. The effectiveness of the oxidants and reductants each depend on their concentrations relative to the other slurry components. As a result, Equation 6 is normalized by the total weight percent solids of the slurry feed (T). This particular form of the model has been used to describe the reduction/oxidation state of glasses from a number of different scaled melters as well as sealed crucible testing from pour stream samples taken directly from DWPF. The fit of the data to the Electron Equivalents model is shown in Fig. 3. The form of the Electron Equivalents model depicted in Equations 5 and 6 is the form currently used in DWPF to estimate the reduction/oxidation of melter feed.

### **In-situ Evaluation and Validation of Reduction/Oxidation State of Melter Feed**

The Defense Waste Processing Facility (DWPF) cannot wait until the melt or waste glass has been made to assess its acceptability. Therefore, the acceptability decision, which includes evaluation of glass quality as well as the reduction/oxidation state of the melter feed, is made on the upstream process, rather than on the downstream glass product. That is, it is based on statistical *process* control rather than statistical *quality* control. For the reduction/oxidation model, the control of feed reductants and oxidants occurs in the SRAT as shown in Fig. 1. Furthermore, since in-situ measurements of  $Fe^{2+}$  and  $Fe^{3+}$  in the melter feed are difficult, the use of the Electron Equivalents model as described previously allows for an easy in-situ estimation of the reduction/oxidation state of the glass through measurement of the anion and elemental composition. For example, the reduction/oxidation of the melter feed is adjusted during the SRAT cycle using measurements of the anion and elemental composition of the sludge feed along with information and projections for the remainder of SRAT and SME processing (i.e. feed forward process control). The Slurry Mix Evaporator is the final evaluation for the actual reduction/oxidation state of the melter feed prior to sending the material on to the melter. If necessary, additions of formic and nitric acid can be made to the SME product to adjust the reduction/oxidation state of the feed.

Since sludge macrobatches processed in the DWPF can have markedly different compositions, the applicability of the Electron Equivalents model as a control strategy for the DWPF is validated through extensive simulant testing. In most cases, the Electron Equivalents model has been validated with no updates required. However, unusual compositions in of reductants and oxidants in a particular macrobatch may require the need to update the model. For example, higher manganese concentrations had been experienced in the early projections of DWPF

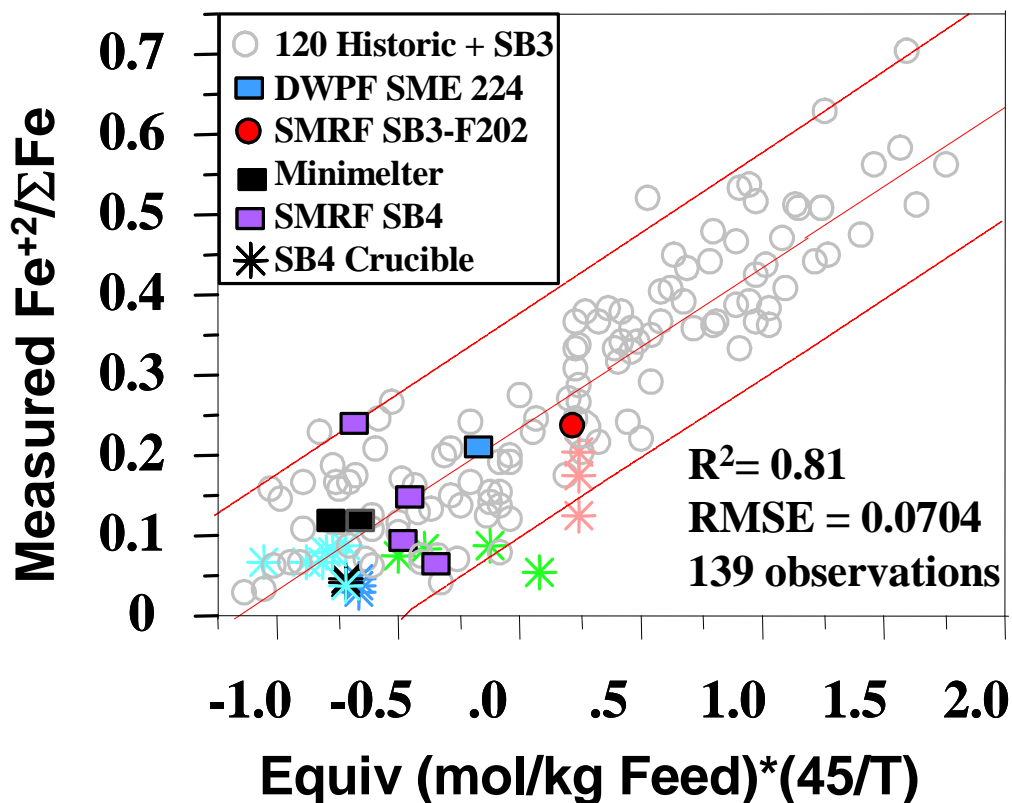


Fig. 3. Relationship between the electron equivalents model given by equation 6 and the measured reduction/oxidation ratio ( $Fe^{2+}/\Sigma Fe$ ) from various experimental studies.

macrobatch 5 compositions than during the 2003 processing of macrobatch 4. During simulant melt rate testing of macrobatch 5 feed simulants, the existing Electron Equivalents model predicted a reduction/oxidation target of  $Fe^{2+}/\Sigma Fe$  of 0.2 but produced glasses that were overly oxidized (i.e.  $Fe^{2+}/\Sigma Fe \sim 0$ ). This observation prompted a change in the number of electrons transferred from -2 to -5 for the manganese term [7].

If required, a glass pour stream sample can be procured during processing to evaluate the actual reduction/oxidation of the sample for further validation of the Electron Equivalents model and control strategy. Samples are delivered to the Savannah River National Laboratory for evaluation. The glass pour stream samples are pulverized and a portion of the sample treated with an acid mixture containing ammonium vanadate. Each sample is analyzed using an ultraviolet/visible spectrometer, and is measured in triplicate. The Environmental Assessment (EA) glass is also treated and measured as an internal check of the reduction/oxidation state measurement. Results from these experiments can be compared to the reduction/oxidation state as predicted based upon the Electron Equivalents model and measurements of the anion and elemental composition obtained during the corresponding SME batch.

#### Impact of Future Facility Changes on the Reduction/Oxidation State of the Glass

Just like compositional changes of the incoming feed stream can require alteration of the reduction/oxidation control strategy at the DWPF, fundamental flowsheet changes to the process

can also require refinement. Currently, the Savannah River Site is pursuing initiatives to improve the overall throughput of the DWPF to accommodate a more aggressive plan to disposition waste from the Tank Farms. Notable improvements which have the potential to impact the reduction/oxidation state of the glass include the addition of bubblers to the melter to improve melt rate [8], and future implementation of an alternate reductant, which reduces or eliminates the use of formic acid from the facility.

A challenge presented with the installation of melter bubblers is the impact of the bubbling medium on the reduction/oxidation state of the glass. Particularly, any impact to the reduction/oxidation state of the glass which takes place following SRAT and SME processing (where the reduction/oxidation state is controlled) must be taken into account. Currently, argon is utilized as the bubbling medium. As evident from glass pour stream samples taken following implementation of bubbling in the melter, argon appears to have a slight reducing effect in the melt pool [9]. To accommodate for the apparent reducing effect of bubbling with argon, the reduction/oxidation state targeted for the melter feed was moved to a more oxidized state (i.e. from  $\text{Fe}^{2+}/\Sigma\text{Fe} = 0.2$  to 0.1) [10]. Currently, work is ongoing to determine the quantitative impact of argon on the reduction/oxidation state of the final waste form.

Another initiative currently ongoing is reduction or replacement of formic acid with an alternate reductant, currently identified as glycolic acid. The purpose of the work is to reduce or eliminate the use of formic acid in the facility, which is known to undergo catalytic decomposition during the SRAT and SME processes, producing hydrogen as a by-product. Clearly, the Electron Equivalents model currently used will require modification to capture the chemistry ongoing with the use of glycolic acid prior to implementation. Currently, work is being done to understand the chemistry of the new flowsheet more clearly, and to develop a new Electron Equivalents model.

## CONCLUSIONS

The reduction/oxidation state of the glass is an important parameter to the operation of the Defense Waste Processing Facility. Control, evaluation, and validation of the reduction/oxidation state of the glass is of particular importance for melter operation. Melter feed which is too oxidizing can negatively impact production, while feed which is too reducing can result in catastrophic failure of the melter. Control strategies for the reduction/oxidation state of the glass have been developed and evolved over the last 20 years to provide a current strategy which is both accurate and robust.

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