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RADIOACTIVE WASTE IN BOROSILICATE GLASS:
PILOT SCALE DEMONSTRATIONS (U)**

by

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ABSTRACT

The Integrated DWPF Melter System (IDMS), operated by the Savannah River Laboratory, is a pilot scale facility used in support of the start-up and operation of the Department of Energy's Defense Waste Processing Facility. The IDMS has successfully demonstrated, on an engineering scale (one-fifth), that simulated high level radioactive waste (HLW) sludge can be chemically treated with formic acid to adjust both its chemical and physical properties, and then blended with simulated precipitate hydrolysis aqueous (PHA) product and borosilicate glass frit to produce a melter feed which can be processed into a durable glass product. The simulated sludge, PHA and frit were blended, based on a product composition program, to optimize the loading of the waste glass as well as to minimize those components which can cause melter processing and/or glass durability problems. During all the IDMS demonstrations completed thus far, the melter feed and the resulting glass that has been produced met all the required specifications, which is very encouraging to future DWPF operations. The IDMS operations also demonstrated that the volatile components of the melter feed (e.g., mercury, nitrogen and carbon, and, to a lesser extent, chlorine, fluorine and sulfur) did not adversely affect the melter performance or the glass product.

INTRODUCTION

The Defense Waste Processing Facility (DWPF), located at the Savannah River Site (SRS), will be the United States' first facility to immobilize high-level radioactive waste (HLW) in a borosilicate glass matrix for ultimate storage in an off-site geologic repository. The Savannah River Laboratory (SRL) operates two engineering-scale facilities to support the DWPF: the Precipitate Hydrolysis Experimental Facility (PHEF) and the Integrated DWPF Melter System (IDMS). The PHEF is one-fifth scale and used to evaluate the Precipitate Hydrolysis Process. It also supplies the Precipitate Hydrolysis Aqueous (PHA) product to the IDMS. The IDMS is used to evaluate the DWPF melter along with its feed preparation and offgas treatment systems. The melter system is one-ninth scale, whereas the feed preparation system is one-fifth scale.

The primary purpose of this paper is to present some of the results obtained from the IDMS engineering scale facility [1, 2], where simulated HLW sludge is chemically processed and then blended with simulated PHA and borosilicate glass frit to produce a melter feed which is processed

into a durable glass product. The results from utilizing a product composition program [3], which determines the amount of each feed material (sludge, PHA and frit) to blend together in order to achieve the desired glass properties, are also presented. Compositions of the sludge, PHA and Frit 202 are given along with the composition of the resulting glass and its properties.

Of the components which enter the system via the sludge, PHA and frit, only mercury, carbon and nitrogen are not incorporated in the glass matrix, as these elements and their compounds are too volatile. Also, the volatility of chlorine, fluorine and sulfur somewhat limits their concentration in the glass. These volatile components can cause problems with the melter system and with the chemical and physical properties of the glass product [4, 5]. Moreover, carbon and nitrogen compounds control the redox potential of the melter feed [5, 6]. Therefore, a secondary purpose of this paper is to describe the immobilization process in detail to exemplify the steps which can have a marked effect on the performance of the melter system and the glass product, and to illuminate the sources of carbon and nitrogen in the feed materials.

EXPERIMENTAL FACILITIES AND MATERIAL SIMULANTS

Melter Feed Preparation and Melter Systems

The IDMS feed preparation and melter systems have been described in detail elsewhere [1, 2]. Therefore, only a brief description of the equipment and its purpose are given. It is worth noting, however, that the IDMS is painstakingly designed to be prototypic of the DWPF not only with respect to the process characteristics but also with respect to the materials of construction.

The IDMS feed preparation system is shown in Figure 1. This system consists of the Sludge Receipt and Adjustment Tank (SRAT), process water condenser, mercury decanter and chilled

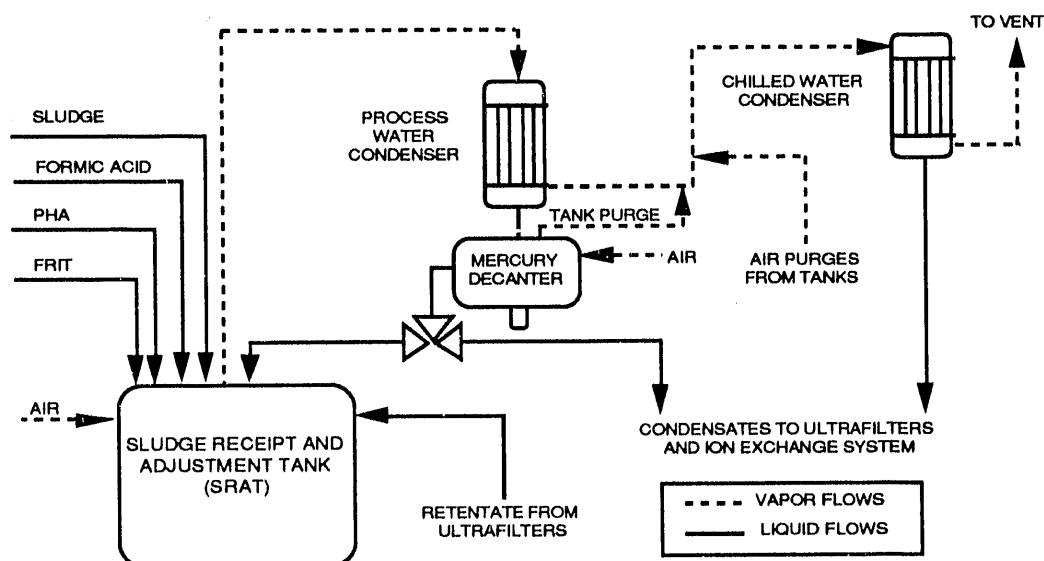


Figure 1. IDMS feed preparation system.

water condenser. The SRAT is equipped with an agitator, steam and cooling water coils, and an

air line which enters the SRAT through a side port for purging the SRAT vapor space. It should be noted that in the IDMS, all materials are added to and processed in the SRAT. This procedure is contrary to that used in the DWPF, which utilizes two tanks-the second tank is for frit addition and concentration (see below and Figure 1). The process water condenser operates at 25 to 50 °C. The condensate from this condenser passes through the mercury decanter and then either back to the SRAT during total reflux or to a condensate tank during concentration. The mercury decanter is designed to collect elemental mercury in a sump for subsequent removal from the process. The non-condensable offgases, after leaving the process water condenser, pass through the chilled water condenser, which is designed to reduce the dew point of the offgas to 10 °C to minimize the release of mercury to the atmosphere. Prior to entering the chilled water condenser, vent streams from several other air-purged tanks also enter the offgas system.

The IDMS melter system, shown in Figure 2, is comprised of the melter, Melter Feed Tank (MFT), and melter offgas system. The melter offgas system consists of the following

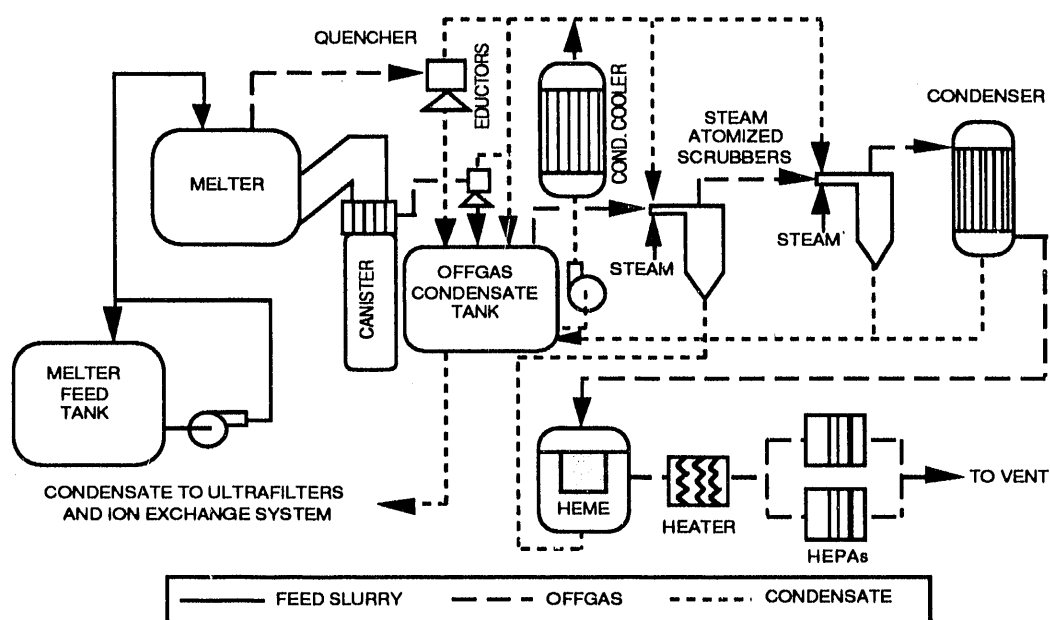


Figure 2. IDMS melter and offgas system.

equipment: the Offgas Film Cooler (OGFC) to reduce deposits at the entrance to the offgas system; the film cooler brush to clean the OGFC; the quencher (venturi scrubber) to cool the offgas and remove large particulates; the Offgas Condensate Tank (OGCT) to disengage the liquids and gases; the two-stage Steam Atomized Scrubbers (SAS) to remove submicron particulates and the condenser to reduce the dew point to 10 °C; the High Efficiency Mist Eliminator (HEME) to remove fine mists and particulates; the High Efficiency Particulate Air (HEPA) Filters (including a preheater) to remove trace particulates; and the blower.

The IDMS melter is a refractory lined, cylindrical tank operated at a glass temperature of about 1,150 °C. It has a 61 cm inner diameter, which gives a melt pool surface area approximately

one-ninth that of the DWPF melter. The melter is used to remove water from the feed by evaporation, react the feed components, and melt the solids to form a homogeneous glass pool that can be poured into steel canisters. The purposes of the offgas system are to maintain a negative pressure in the melter plenum, provide adequate air for combustion in the plenum (which is normally maintained at about 800 °C, treat the offgases to remove condensibles and particulates, and provide the vacuum required to initiate and control the pouring of glass. The melter offgas consists of steam, non-condensable gases from sludge decomposition, air from inleakage and purges, mercury vapor, and particulate matter from entrainment and volatilization.

Simulated HLW Sludge and PHA, and Frit 202

The simulated sludge and PHA described here contain reference levels of the major non-radioactive components of the Savannah River Site (SRS) HLW, including halides, sulfates and mercury but no noble metals. Table 1 displays the composition of the major components of the nominal "Batch 1" type simulated sludge. This type of sludge is characteristic of the first DWPF

Table 1. Cation and Anion Content of Simulated "Batch 1" Type Sludge (wt% dry)

| | | | | | | | |
|----|--------|----|-------|---------------------------------|-------|------------------|-------|
| Al | 6.562 | Mn | 4.687 | SO ₄ ⁻² | 0.665 | Cl ⁻¹ | 0.980 |
| Ba | 0.163 | Na | 5.681 | PO ₄ ⁻³ | 0.092 | F ⁻¹ | 0.124 |
| Ca | 2.161 | Nd | 0.249 | CO ₃ ⁻² | 2.921 | I ⁻¹ | 0.018 |
| Cr | 0.179 | Ni | 1.546 | NO ₂ ⁻¹ | 7.332 | OH ⁻¹ | 0.738 |
| Cs | 0.005 | Pb | 0.278 | NO ₃ ⁻¹ | 0.504 | | |
| Cu | 0.105 | Si | 1.442 | | | | |
| Fe | 22.803 | Sr | 0.060 | Organic Carbon (wt% wet) < 0.05 | | | |
| Hg | 1.588 | Zn | 0.185 | Total Solids (wt% wet) 15.4 | | | |
| K | 0.248 | Zr | 0.768 | Insoluble Solids (wt% wet) 12.9 | | | |
| Mg | 0.156 | | | | | | |

operations with actual SRS HLW. Note that the sludge contains a significant amount of nitrite as well as nitrate. A typical composition of the PHA product produced in the PHEF is given in Table 2. A high level of copper and a considerable amount of formate are present in the PHA product: formic acid along with a copper catalyst are used in the PHEF to hydrolyze tetraphenylborate to benzene [7]. Hydrolysis causes numerous side reactions which produce a variety of high and low boiling organic compounds (mostly benzene derivatives). The major organic compounds produced are listed in Table 2. Also, the PHA, similar to the sludge, contains a considerable amount of nitrate. The borosilicate glass frit (Frit 202) is comprised of (in wt%): SiO₂ (77.0), Na₂O (6.0), B₂O₃ (8.0), Li₂O (7.0) and MgO (2.0). Note that it is blended with water and a small amount of formic acid prior to being blended with the sludge-PHA mixture.

Each of these three feed materials contains a significant amount of formate which remains in the melter feed. Approximately 50% comes from the PHA, 45% from the sludge and 5% from the frit slurry. Formate is the major component of the melter feed which influences the reducing

Table 2. Cation, Anion and Organic Content of Simulated PHA (wt% dry)

| | | | | | | | |
|--|-------|---|-------|--|--------|------------------|-------|
| Al | 0.044 | Mg | 0.032 | SO ₄ ⁻² | 0.278 | Cl ⁻¹ | 0.158 |
| B | 3.145 | Mn | 0.160 | COOH ⁻¹ | 25.221 | F ⁻¹ | 0.008 |
| Ba | 0.001 | Na | 8.675 | NO ₂ ⁻¹ | 24.089 | | |
| Ca | 0.091 | Ni | 0.049 | | | | |
| Cu | 0.473 | P | 0.001 | Organic Carbon | | 7.0 | |
| Cr | 0.002 | Si | 0.052 | Inorganic Carbon | | 0.116 | |
| Cs | 0.552 | Sr | 0.002 | Total Solids (wt% wet) | | 6.0 | |
| Fe | 0.336 | Ti | 1.108 | | | | |
| K | 8.553 | Zn | 0.011 | | | | |
| C ₆ H ₆ | 0.002 | (C ₆ H ₅) ₂ C ₆ H ₄ | 0.124 | C ₆ H ₅ C ₆ H ₄ OH | | 0.208 | |
| (C ₆ H ₅) ₂ | 0.163 | (C ₆ H ₅) ₂ NH | 0.180 | C ₆ H ₅ NO ₂ | | 0.059 | |
| C ₆ H ₅ OH | 4.683 | C ₆ H ₅ NHCHO | 0.717 | C ₆ H ₅ NO | | 0.069 | |
| C ₆ H ₅ B(OH) ₂ | 0.002 | C ₆ H ₅ NH ₂ | 0.710 | | | | |

potential of the glass melt and can ultimately cause problems with the performance of the melter. The HLW sludge and PHA both contain nitrate which also remains in the melter feed (some of the nitrite in the sludge is converted to nitrate during processing). In this case, approximately 75% comes from the PHA, 20% is produced during processing and 5% from the sludge. Nitrate is the major component of the melter feed which affects the oxidizing potential of the glass melt and can also cause problems with the performance of the melter. The formate and nitrate levels thus control the potential of the melter feed and glass properties [5, 6]. Bickford and Choi [5] and Ramsey, *et al.* [6] treat this topic along with the role of organics in controlling both the glass properties and melter performance. These topics are briefly discussed in this work, but only as related to results from IDMS operations.

DISCUSSION OF IDMS RESULTS

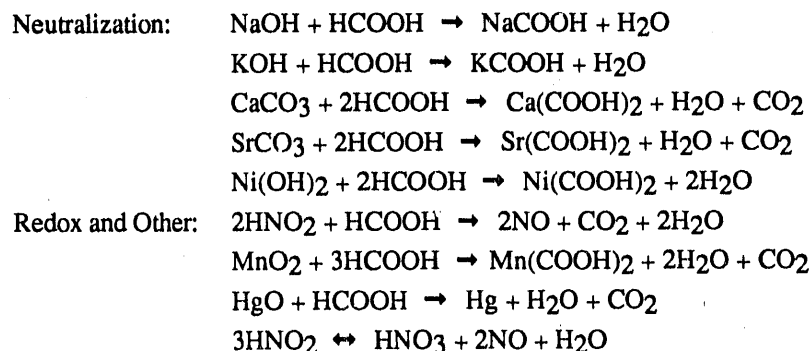
Melter Feed Preparation

First, approximately 3,800 liters of simulated sludge are transferred to the SRAT. Mercury is added to the SRAT as mercuric nitrate (Hg(NO₃)₂), which forms mercuric oxide (HgO) upon contact with the alkaline sludge (HgO is the form expected in actual SRS HLW). After mercury is added, the SRAT is heated to between 93 and 96 °C in order to add 150 liters of formic acid. The 90 wt% solution of formic acid is added at 0.4 liters/min/1,000 liters of sludge. After the formic acid is added, the SRAT is heated to boiling and refluxed for 6 hours to allow time for the slower reactions to proceed and to steam strip mercury. Next, approximately 7,200 liters of PHA are added at 7.6 liters/min and, at the same time, condensate is removed from the system thereby maintaining the SRAT at a constant level. This step requires 13 hours during which time more mercury stripping occurs. Upon completion of the PHA addition and concentration period, 1,360 kg of Frit 202 in the form of a 50 wt% frit-water slurry are added to the SRAT. Eight liters of formic acid are added to the frit-slurry to minimize dissolution and gelation of the frit. The frit-slurry is added to the SRAT at 80 liters/min while in the concentration mode. After this addition, 10 hours are required to concentrate the sludge/slurry to the original volume of 3,800 liters, which corresponds to 45 to 50 wt% solids. This final product is sampled to ensure it meets the process control requirements. It is then transferred to the MFT and fed to the melter.

The average melter feed rate is 30 liters/min, while the nominal glass pour rate is 1 kg/min.

Formic acid is used during melter feed preparation to adjust the sludge via a series of acid-base and redox reactions. The major reactions of formic acid are listed in Table 3. This adjustment

Table 3. Major Reactions of Formic Acid with Simulated Sludge Components



includes the neutralization of metallic carbonates and hydroxides to improve the rheology of the sludge, the reduction of mercury to its metal for removal by steam stripping, and the reduction of manganese to improve the melter operation by decreasing foaming. Note that the methods used to determine the amount of formic acid required are given elsewhere [7, 8].

A typical offgas composition profile produced during formic acid addition and reflux is shown in Figure 3. Although the major reactions all proceed in parallel, one or two of them tend to predominate at any one time. The first reactions to occur during formic acid adjustment are the neutralization of soluble hydroxides (NaOH and KOH). The next reactions to occur are neutralizations of insoluble Ca and Sr carbonates, which evolve CO_2 . A small amount of NO_x (NO and NO_2) is also evolved, which is probably due to the reaction of nitrous acid with formic acid or the self-decomposition of nitrous acid (see Table 3). Note that nitrous acid is formed by the protonation of nitrite by formic acid. Once most of the neutralization reactions begin to subside and CO_2 and NO_x concentrations have peaked, the production of CO_2 and NO_x again increase because of the increased contribution from the redox reactions. At this time, the Hg also begins to be reduced as evidenced by the presence of Hg in the offgas condensate.

An offgas profile for the PHA addition and concentration steps is not presented here because only a small amount of CO_2 is evolved during this step of melter feed preparation. The CO_2 is partly produced from the continuation of the slower reactions ($\text{Ni}(\text{OH})_2$ and MnO_2) in the formic acid-treated sludge. It is also partly produced from the PHA itself, where copper and other metals are suspected of undergoing redox reactions with formate.

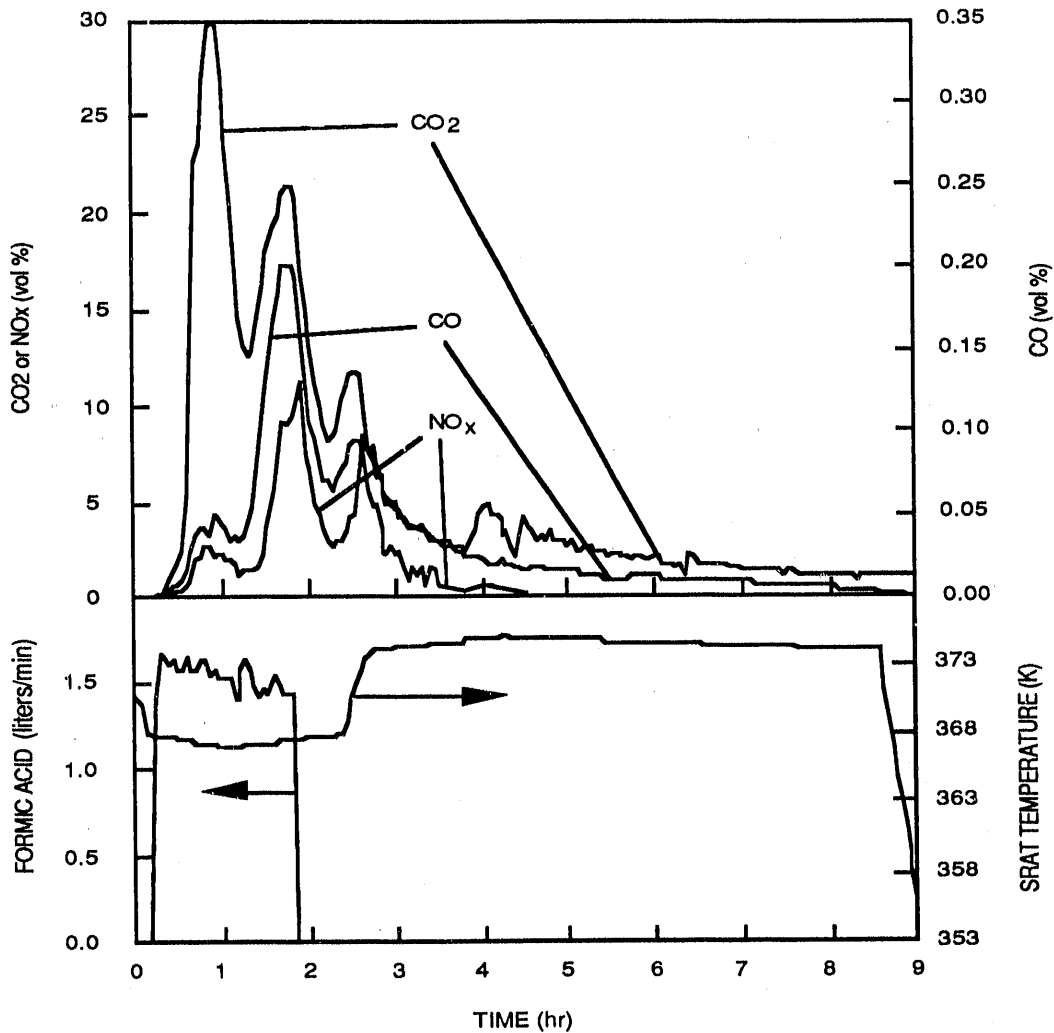
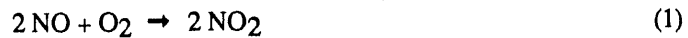


Figure 3. Typical composition of offgas during formic acid addition and reflux.

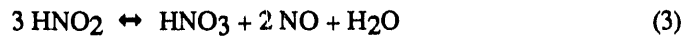
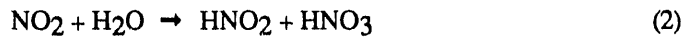
Moreover, during PHA addition and concentration, a significant amount of organics enter the SRAT, besides the additional formate (see Table 2). It is estimated that 85% of the phenol is removed during concentration and ends up in the condensate. The remaining organics are fed to the melter but make up only a small fraction of the total carbon, as most of the carbon is in the form of formate. Nevertheless, they can impact the melter performance [5, 6].

The offgas from the SRAT contains predominantly air, NO and CO₂. However, some NO₂ is present and is most likely formed from the following gas phase reaction of NO with O₂:



This reaction occurs in the vapor space above the SRAT and in the offgas lines and causes

reactions to occur in the offgas condensate because NO₂ is easily scrubbed from the offgas lines with condensing water vapor. The major reactions in the offgas condensate are those that form nitrous and nitric acids:



These reactions cause the condensate from the process water condenser to be very acidic: pH ranges from < 1 to about 4. Figure 4 shows the nitrous, nitric and formic acid concentrations in the condensate and the NO_x concentration during a typical IDMS demonstration. The acid concentrations are the highest when the rate of generation of NO_x is at its highest.

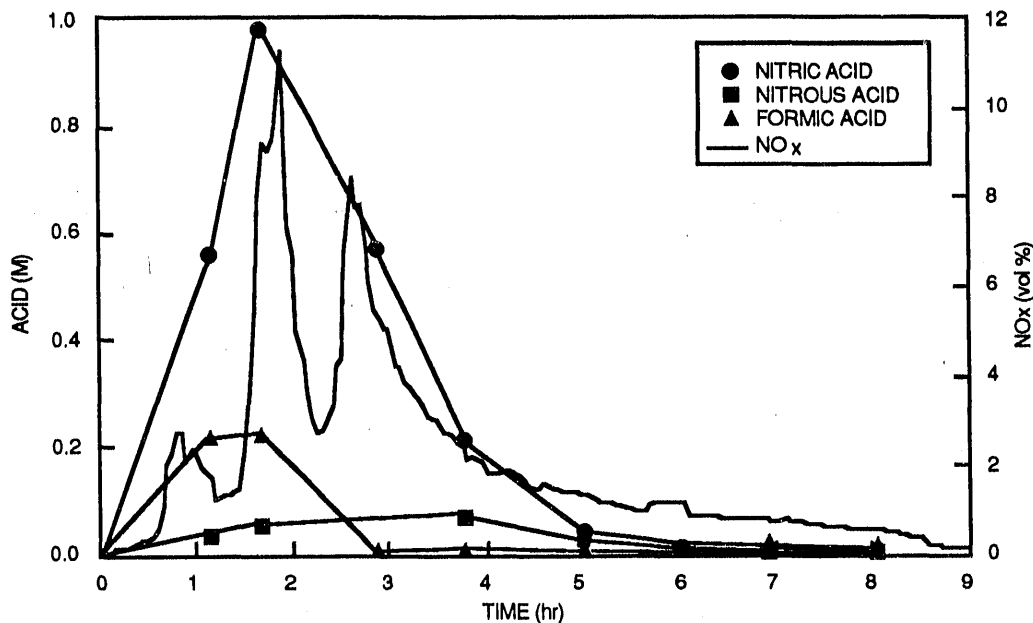


Figure 4. Typical acid concentration in offgas condensate during formic acid addition and reflux.

The amount of nitrate initially in the sludge varies depending on the exact batch of sludge used and the processing history of the tank, but is generally around 2,000 mg/liter. Based on the above information and the last reaction shown in Table 2, a significant amount of nitrate is produced during formic acid addition and reflux, especially since the acidic condensate is recycled back to the SRAT during this period. However, the contribution from each source varies substantially during different IDMS demonstrations. After formic acid adjustment, the nitrate concentration increases to between 10,000 and 12,000 mg/liter, and accounts for between 10 and 20% of the nitrate fed to the melter. Based on previous information, this increase in nitrate concentration in the sludge can impact the melter performance.

Mercury Processing

Mercury is one of the few sludge components which does not become immobilized in the glass as it is too volatile. Moreover, mercury and some of its compounds are known to be corrosive at the elevated temperatures which exist in the melter offgas system. Thus, the immobilization process is designed to remove the mercury from the sludge before it is fed to the melter.

The formic acid-reduced elemental mercury is continuously steam stripped from the sludge during formic acid addition and reflux, and also during PHA addition and concentration. It is condensed in the process water condenser and collected in a sump in the bottom of the mercury decanter, where it is subsequently removed from the process. By design, the final concentration of mercury in the sludge should be around 0.45 wt%. In numerous IDMS demonstrations, the end point concentration of the sludge ranged from 0.08 to 0.25 wt%, well exceeding the design concentration. These results are very encouraging because, during formic acid addition and reflux, a considerable amount of Hg is recycled back to the SRAT instead of being collected in the sump as Hg readily dissolves in nitric/nitrous acid solutions (Equ. 2 and 3). The concentration of mercury in the condensate, for the most part, follows the concentration of nitrate (see Figure 4). Nevertheless, approximately 80 to 90% of the mercury originally present in the sludge is removed. The mercury remaining in the sludge, which is thus present in the melter feed, exits with the melter offgas since mercury and its compounds decompose at temperatures $\ll 1,150\text{ }^{\circ}\text{C}$.

Mercury in the melter offgas may be in the form of a complex mixture of halides, oxides and metal. Mercuric halides are very corrosive, especially at elevated temperatures. However, analysis of the condensate indicates that virtually all of the Hg is soluble and little Hg_2Cl_2 (calomel) is formed. Analysis of filter papers from an offgas sampling system also show no evidence of mercury solids (Hg_2Cl_2). Formation of Hg_2Cl_2 is a concern since it can accumulate on the HEME and shorten its life. The absence of mercury solids in the melter offgas system is most likely due to the fact that the amount of mercury entering the melter is a factor of 20 to 100 times less than anticipated because of the high removal efficiency during melter feed preparation.

Melter Feed Processing

The melter feed is slowly fed to the melter through a narrow tube and is sprayed on top of the cold cap. Due to the high temperature in the melter plenum ($800\text{ }^{\circ}\text{C}$), much of the water is immediately vaporized as it exits the melter feed tube. The more volatile organics are also immediately converted to CO_2 and H_2O , and CO and H_2 as the water-gas shift reaction occurs at the melter plenum temperature. However, the considerable amount of formate which enters the melter is not oxidized until it enters the cold cap. Moreover, about 60% of the nitrate which is formed in the sludge during formic acid addition is converted to NO_x , but also not until it enters the cold cap (it is thought that the remainder of the nitrate gets converted to O_2 and N_2).

Typically, 40 to 60 g/liter each of formate and nitrate are present in the melter feed. Therefore, these two compounds can have a significant effect on whether the glass melt (or melter feed) has a reducing or oxidizing potential. A melter feed which is too reducing can cause metals to precipitate out of the glass melt and short the melter electrodes by pooling on the floor of the melter. The presence of the other organics in the melter feed (see Table 2) can also cause a reducing glass melt as well as other melter performance problems. This topic is beyond the scope of this work and, as stated earlier, is treated elsewhere [5, 6].

One measure of the redox potential of the melter feed is based on the ratio of Fe⁺² to Fe⁺³ (Hsu [8] shows how this ratio is related to the formate and nitrate concentrations in the melter feed). An acceptable range for this ratio is between 0.1 to 0.5, as shown in Table 4. If the ratio is

Table 4. Control Glass Properties from Three IDMS Demonstrations

| Glass Property | Acceptable Range | IDMS Demonstration | | |
|--------------------------------------|-----------------------------------|--------------------|-------|-------|
| | | 1 | 2 | 3 |
| Liquidus (°C) | ≤ 1050 | 1043 | 985 | 931 |
| Viscosity (Poise) | 20 - 100 | 40 | 67 | 97 |
| Durability (kcal/mol) | $\Delta G_{\text{hyd}} \geq -7.0$ | -5.98 | -5.09 | -4.65 |
| TiO ₂ (wt%) | ≤ 1.0 | 0.62 | 0.59 | 0.37 |
| Cr ₂ O ₃ (wt%) | ≤ 3.0 | 0.20 | 0.19 | 0.11 |
| P ₂ O ₅ (wt%) | ≤ 0.3 | 0.08 | 0.20 | 0.42 |
| Fe ⁺² /Fe ⁺³ | 0.1 - 0.5 | 0.03 | 0.16 | 0.14 |

below this range, the melter feed or glass is considered oxidizing and vice versa if it is above this range. As shown in Table 4, the glasses produced during IDMS demonstrations 2 and 3 are only slightly reducing, whereas that produced during IDMS demonstration 1 is oxidizing. Apparently, the excess organics from the PHA, compared to the amount of formate, do not have a significant effect on the reducing potential of the glass melt. However, the oxidizing glass most likely resulted from the excess nitrate produced during melter feed preparation which may not have been accounted for at that time. These results indicate that the excess nitrate (about 15 to 20% of the total nitrate in the melter feed) can possibly affect the oxidizing potential of the glass melt, in agreement with the work by Ramsey, *et al.* [6].

Glass Composition Control

The algorithm used to control the glass product composition in the IDMS is similar to that planned for the DWPF [3]. The procedure requires the following steps: 1) select a target blending scheme for the percentages of sludge oxides, PHA glassformer oxides and frit oxides, based on the compositions of each of these major materials, to give a final glass product within the specified boundaries; 2) determine the operational data required to process the batch (i.e., volumes to transfer, formic acid requirement, etc.); and 3) verify that the final product is within the prescribed specifications, and if necessary add trim chemicals to adjust. For an IDMS demonstration, sludge, PHA and Frit 202 are blended to achieve the following oxide mixture: 28 wt% waste oxides, 8 wt% PHA glassformer oxides and 64 wt% frit oxides.

The resulting control glass properties for three IDMS demonstrations and the acceptable glass property ranges are summarized in Table 4. From this table it is seen that both the liquidus temperature (Run 1) and the high viscosity (Run 3) processing limits are approached during these runs (the oxidizing glass produced during run 1 is discussed above). It should be noted that these three runs are not planned as a rigorous demonstration of the DWPF product control algorithm. Nevertheless, they show that the product composition program is sufficient for providing the amounts of each material to be blended (sludge, PHA and frit) in order to make an acceptable product. The use of the product composition program has also been demonstrated using actual HLW, but only on that which was processed using a bench scale apparatus [10].

Glass Product

A typical material balance around the melter system (i.e., melter feed to glass) for selected elements and anions is shown in Table 5. The average value from numerous samples of each

Table 5. Cation and Anion Content of Melter Feed, Glass and OGCT Condensate

| | kg/100 kg Glass | | | | | kg/100 kg Glass | | | |
|----|-----------------|-------|-------|-------|-------------------------------|-----------------|--------|-------|-------|
| | MFT | Glass | OGCT | %* | | MFT | Glass | OGCT | %* |
| Al | 2.533 | 2.481 | 0.001 | 98.0 | Na | 6.992 | 7.092 | 0.014 | 101.4 |
| B | 2.300 | 2.279 | 0.009 | 99.5 | Nd | 0.165 | 0.183 | 0.000 | 110.9 |
| Ba | 0.071 | 0.072 | 0.000 | 101.4 | Ni | 0.543 | 0.585 | 0.000 | 107.7 |
| Ca | 0.823 | 0.877 | 0.002 | 106.6 | P | 0.016 | 0.020 | 0.001 | 125.0 |
| Cr | 0.139 | 0.164 | 0.001 | 118.0 | Pb | 0.109 | 0.126 | 0.000 | 115.6 |
| Cs | 0.280 | 0.180 | 0.003 | 64.3 | Si | 23.630 | 22.567 | 0.003 | 95.5 |
| Cu | 0.175 | 0.197 | 0.001 | 112.6 | Sr | 0.024 | 0.025 | 0.000 | 104.2 |
| Fe | 8.217 | 8.952 | 0.004 | 109.0 | Ti | 0.247 | 0.275 | 0.000 | 111.3 |
| Hg | 0.089 | 0.000 | 0.087 | 0.0 | Zn | 0.069 | 0.053 | 0.001 | 76.8 |
| K | 2.886 | 2.811 | 0.012 | 97.8 | Zr | 0.084 | 0.087 | 0.000 | 103.6 |
| Li | 2.091 | 1.951 | 0.001 | 93.3 | Cl ⁻¹ | 0.527 | 0.2483 | 0.046 | 47.1 |
| Mg | 0.870 | 0.821 | 0.000 | 94.4 | F ⁻¹ | 0.129 | 0.0503 | 0.012 | 39.0 |
| Mn | 1.399 | 1.581 | 0.000 | 113.0 | SO ₄ ⁻¹ | 0.187 | 0.0004 | 0.042 | 0.2 |

* % = 100 (Glass/MFT)

component in the MFT, OGCT and glass product are given. The ratio of each component in the glass to that in the MFT (expressed as a percent) is also shown. This ratio, when significantly different than 100, gives an indication of those components in the melter feed which are volatile. Note that the standard deviation for most of these results is on the order of $\pm 15\%$.

There are significant amounts of B, Ca, Cl, Cs, F, Fe, K, Na, S and Si in the OGCT, which suggests that these components are somewhat volatile (note that entrainment probably causes the first six elements to be in the OGCT). Furthermore, based on the percentages, Cl, Cs, F, S and Zn are quite volatile. Cesium is a concern as it is a radioactive constituent in actual HLW. The melter offgas system (see Figure 2) is designed to remove Cs and other radionuclides. It is reassuring that the decontamination factors across the offgas system are two orders of magnitude better than the design basis [11]. The percentages listed for the anions are quite small, and significant amounts of each are in the OGCT, which suggests that they are extremely volatile. More importantly, the apparent loss of these components from the MFT to the glass product is due primarily to a buildup of matter in the melter offgas lines.

The composition of the material deposited in the melter offgas lines is a mixture of (Na,K,Cs)Cl,F and (Na,K,Cs)SO₄ and (Na,K,Cs)BO₄; there is also evidence of spinel forming elements (Fe, Mn and Cr) [4]. This buildup of material can be detrimental to the performance of the melter as it can cause excessive pressure drop in the offgas system or even plug the offgas lines. However, it is encouraging that during all IDMS operations to date, the effects of materials deposition in the melter offgas lines has been minimal.

The results in Table 5 also show that most of the solids except for mercury, carbon and nitrogen, and to a lesser extent sulfur, chlorine and fluorine, are incorporated in the glass. A typical composition of the glass produced in the IDMS is given in Table 6. About half of the glass is

Table 6. Nominal Composition of "Batch 1" Type Glass (wt%)

| | | | | | |
|--------------------------------|--------|--------------------------------|-------|------------------|--------|
| Al ₂ O ₃ | 4.819 | K ₂ O | 3.474 | PbO | 0.140 |
| B ₂ O ₃ | 7.543 | Li ₂ O | 4.317 | SiO ₂ | 49.630 |
| BaSO ₄ | 0.126 | MgO | 1.400 | SrO | 0.030 |
| CaO | 1.261 | MnO | 2.099 | TiO ₂ | 0.472 |
| Cr ₂ O ₃ | 0.246 | Na ₂ O | 9.829 | ZnO | 0.068 |
| Cs ₂ O | 0.020 | Nd ₂ O ₃ | 0.187 | ZrO ₂ | 0.121 |
| CuO | 0.253 | NiO | 0.765 | | |
| Fe ₂ O ₃ | 13.153 | P ₂ O ₅ | 0.047 | | |

composed of Si and one-eighth as Fe. The remaining 37% of the glass is made up of 19 components which each make up less than 10% of the glass. For example, 8 of the 19 components are each in the glass at a concentration of less than 10%, and the 11 remaining components each make up less than 1% of the glass. Overall, this glass contains approximately 28 wt% waste oxides and meets all the required specifications, as shown in Table 4.

CONCLUSIONS

Based on the product composition program, which optimizes the loading of the waste glass as well as minimizes those components which can cause melter processing and/or glass durability problems, the simulated sludge and PHA, and the frit have been successfully blended and processed in the IDMS. During all the IDMS demonstrations completed thus far, the melter feed and the resulting glass that has been produced has met all the required specifications. Therefore, the IDMS has demonstrated that the product composition program can provide the blending scheme required to produce an acceptable glass, and that similar results can be expected during the DWPF cold chemical runs. Future IDMS operations with simulated sludge spiked with noble metals are planned to determine the effect of the redox potential of the melter feed on the state of the noble metals and the subsequent effect of the noble metals on the melter performance.

The redox potential of the melter feed is controlled for the most part by a balance between the amount of carbon and nitrogen entering the melter. The sources of carbon in the melter feed in the form of formate are: PHA ≈ sludge >> frit slurry. Only the PHA contains an additional carbon source from the hydrolysis of tetraphenylborate, but this carbon accounts for only a small fraction of the carbon entering the melter relative to formate. The sources of nitrogen in the melter feed in the form of nitrate are: PHA > NO₂ → NO₃ > sludge. The sources of the volatile components (Hg, Cl, F and S) are: sludge >> PHA.

The IDMS operations also demonstrated that the volatile components of the melter feed (Hg, C and N, and, to a lesser extent, Cl, F and S) have not adversely affected the performance of the melter or the glass product. Since mercury removal from the sludge during melter feed

preparation far exceeded the design basis, only traces of corrosive forms of mercury have been detected in the melter offgas system. The excess nitrate produced in the SRAT offgas condensate may have caused an oxidizing melter feed; however, the effect has seemingly been accounted for during subsequent operations. The excess organics from the PHA, compared to the formate, also had little effect on the reducing potential of the melter feed. The deposition of volatile materials in the melter offgas system has yet to cause pressure drop or pluggage problems.

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