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by

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ABSTRACT

The vitrification of nuclear waste glasses is presenting unique challenges to glass technologists. On the one hand, the composition of the most important constituent of the glass batch - the waste - may vary widely. On the other hand, the vitrification process itself must be tightly controlled to ensure product quality, public safety, and process reliability.

This has led to several important developments in waste vitrification technology, all aimed at improving process control. These include use of process models, use of artificial intelligence techniques, and improved control and measurement of glass redox.

INTRODUCTION

The nuclear waste glass technologist has a unique challenge [1]. The feed to the glass melter contains most of the elements in the periodic table, and, for the major elements, may vary widely (Table 1). Many of the elements are present in concentrations, or chemical forms, which are hard to dissolve into the glass. The glass products, although of varying composition, must all be durable over the eons of geologic time.

The process which is used must be highly reliable. It will be run behind massive concrete walls several feet thick, where maintenance is limited to whatever tools can be mounted on an overhead crane. All of the glass products must have acceptable durability, because there is no easy way to rework unacceptable glass. Allowable releases of hazardous materials are much more constrained than in conventional glass melting: where releases of 0.01% of a hazardous substance in the feed to a conventional melter might be exemplary in the commercial glass industry, the process to vitrify nuclear waste must be capable of meeting standards 4-5 orders of magnitude more stringent. Thus, the nuclear waste glass technologist must often go beyond conventional glass technology, because of the unique nature of the problems which must be solved. In particular, control of the vitrification process is necessarily very different than control in conventional glass processing.

At the Savannah River Plant (SRP), construction of what will be the world's largest vitrification plant for nuclear waste, the Defense Waste Processing Facility (DWPF), has been underway since 1982 [2]. In this plant, the 33 million gallons of high-level liquid waste currently stored at SRP will be made into a durable borosilicate glass. Once that is done, the DWPF will process waste at the same rate as it is generated at SRP.

In our development of the slurry-fed melting process for the DWPF, we have had to extend conventional glass technology, particularly to en-

sure that the vitrification process will be in control. This paper is focused on several of the unconventional methods we are currently developing.

VITRIFICATION PROCESS

The DWPF process is shown schematically in Figure 1. In the SRP tank farm, the insoluble portion of the waste (called "sludge"), which contains virtually all of the long-lived radionuclides, will be treated with caustic, and then washed with water to reduce the volume of material to be vitrified. The soluble portion of the waste will be treated with sodium tetraphenylborate to remove radioactive cesium. In the DWPF, the tetraphenylborate salts will be reacted with formic acid to remove approximately 90% of the organics. The sludge will also be treated with formic acid, to improve slurry rheology and stability, and to reduce the oxidation state of materials which could cause foaming in the melt.

The sludge slurry will then be mixed with the Cs, B, K, and Ti from the tetraphenylborate precipitation process, and glass forming chemicals (in the form of a pre-melted frit) will be added. The resultant slurry will then be fed directly to a joule-heated glass melter, and converted to a borosilicate glass at 1150°C. This direct slurry feeding is, in itself, one of the major advances in waste vitrification, as has been previously discussed [1]. The glass will be continuously poured, by vacuum, into a stainless steel canister, which will then be welded closed, decontaminated, and stored at SRP [3,4].

PROCESS CONTROL

Remote nuclear processes, such as waste vitrification, place a high premium on reliability. The general approach we are taking is to first identify the variables which are important for process and product reliability. We will then determine the best means to control them, and implement a system of specifications and administrative procedures to ensure that the important process variables are controlled.

Examples of important variables which we have already determined must be controlled for nuclear waste vitrification are listed in Table 2, with the preliminary control limits which have been established. These variables are:

- Glass durability. This is the most important product property. One of the primary reasons glass was chosen as the medium for immobilization of SRP waste was because of its ability to produce a durable product from the full spectrum of wastes at the Savannah River Plant [5]. The specifications established for acceptance of the DWPF glass product by the repository require that the DWPF qualify the vitrification process by demonstrating that glass durability can be controlled, and then verifying that it has been controlled, during production. Durability is defined as the ability to release less than 1 $g/m^2 \cdot d$ (based on Si, B, Na, Li, and Cs), in a 28-day static leach test (MCC-1) in deionized water (see Table 2) [6].

- Glass viscosity. Probably the most important processing property, the viscosity determines the corrosivity and volatility of the melt, and its ability to be poured from the melter [7]. It also plays

an important role in determining the rate of glass production, because it determines how fast dissolved waste can be conveyed away from the cold cap. The lower limit in Table 2 reflects our experience in corrosion testing and long-term melter operation, while the upper limit is derived from our own experience as well as that of our colleagues in Europe.

• Liquidus temperature. The DWPF melter is designed to maintain the glass temperature above 1050°C throughout the melter. If the liquidus is greater than 1050°C, some of the waste will precipitate out of the glass melt [7], potentially plugging the pour spout, and probably leading to enhanced throat and riser wear. In addition, the goal of waste vitrification is to immobilize the waste in glass. If the waste precipitates in the melter, we will have failed to reach our aim.

• Glass redox. If fed directly to the melter without pretreatment, the multi-valent oxides in the waste evolve oxygen during melting, and cause foaming [1]. However, if, for any reason, the melts are too reduced, metals such as nickel and ruthenium can precipitate in the melter, and can lead to shorting of electrodes, or accelerated corrosion of the melter bottom.

COMPOSITION - PROPERTY MODELS

There are two types of models which we are developing and using for process control purposes: composition—property, and process simulation. Composition—property models are based on the assumption that the particular property (e.g. durability) can be effectively considered to be only a function of the chemical composition of the glass. Control of variables for which this is a valid assumption then becomes simply a matter of control of the chemical composition. For these important variables (durability, viscosity, liquidus), both physical and chemical control systems are ready to be used once operations begin in the DWPF. For all of these, however, the control of the chemical composition of the glass will be the key to maintaining a reliable process.

For durability, viscosity, and liquidus, this will be done by developing models of these properties as a function of composition, and then treating the limits in Table 2 as constraints on the allowed composition. Thus, these models are the means by which we will convert the glass property limits in Table 2 into process control limits.

Glass Durability

The model developed for glass durability has been described in detail elsewhere [8-12]. Essentially, it relates the measured release of material under specified test conditions to the free energy of hydration of the glass. It treats the durability as an additive property of composition of the form

$$\log\ (\text{release}) = \sum_i x_i \cdot \Delta G_i^{\circ}(\text{hydration})$$

where x_i is the mole fraction of component i in the glass, and ΔG°_i(hydration) is the free energy of hydration of component i. This model has been extensively tested, and been shown to be applicable to an extremely wide range of silicate glasses [8-12].

Glass Viscosity

Several models are being evaluated for glass viscosity. In general, all are of the form

$$\log \eta = \sum_i x_i \cdot \gamma_i$$

where η is the viscosity, x_i is the mole fraction of component i in the glass, and γ_i is a coefficient which varies for each component in the glass. Two forms of γ_i are currently being investigated. In the first, γ_i is independent of temperature, and the viscosity thus computed is only true for a fixed temperature (e.g. 1150°C). The second approach is more ambitious, in that it assumes that γ_i is a function of temperature (initially assumed to be Arrhenian). This approach thus produces a viscosity function which allows the calculation of viscosity at any temperature. The choice between these two approaches will depend on which more accurately represents experimental data.

Glass Liquidus

Two very different approaches are being taken to develop compositional models of the glass liquidus temperature. In the first, empirical models of the liquidus temperature as a function of composition have been developed and are being used to plan for initial DWPF operation. These models all point to the iron content of the glass as the most important determinant of the liquidus, and are less sensitive to variations in other components. However, these models cannot be extrapolated to other waste types very easily.

A more ambitious long-term solution is to develop waste glass specific phase diagrams which reflect known phase equilibria from the literature. This approach, though more difficult to establish initially, potentially will make it much easier to determine how to operate the process several years, or even decades, from now, when the waste composition may be radically different than it is now.

CONTROL OF GLASS COMPOSITION IN THE DWPF

A model simulating the entire DWPF process has been developed to determine what the composition of the final glass will be, given initial inputs. These inputs are the frit composition, the sludge composition, the composition of the material from the tetraphenylborate process, and the amounts of each previously used. The various compositional models will then be used to determine whether the glass will be acceptably durable, and can be reliably processed. If the answer to either is no, the various inputs will be varied until the final glass composition meets all of the constraints. The values of the input amounts of each stream (frit, sludge, and tetraphenylborate material) will then become the initial set points for the process. The simulation is currently being used to indicate where possible trouble points may occur.

When processing begins, the key compositional variables will be

measured, and adjusted as necessary, at certain points in the process called the chemical composition hold points (Figure 2). The feed will not be allowed to be transferred to the next process step until it is within the process control limits set for each of these hold points.

Samples will also be taken after each of these hold points which will allow tuning of the process simulation. For example, the initial sludge composition is not very well known because of our limited ability to obtain samples from the tank farm. However, we will gain more precise knowledge about the composition of the sludge during processing, because we will be processing the same sludge batch for at least two years. Thus, initial set points may be set slightly lower in terms of sludge loading reflecting the imprecision of our knowledge. The sludge loading could then gradually be increased, as we reduce our uncertainty about the actual composition. Samples of actual DWPF glass, taken during pouring, will also allow us to tune our model of glass durability.

GLASS REDOX AND PROCESS SIMULATION

For properties such as glass redox, control of the chemical composition of the glass is not effective in achieving control of the variable. In this case, simulations of the processes controlling glass redox must be developed and validated, and then used to determine effective control schemes.

Two different paths are being followed for glass redox control. In the first, experimental correlations are being developed between the logarithm of the oxygen fugacity, and the equilibria among various oxidation states of multivalent species [13-15]. These empirical correlations are being used to define limits for the glass redox state. An example of this is provided by the excellent experimental work of Schreiber, and its use for control by Bickford [16].

During operation, samples of feed will be taken, and melted in a closed crucible to provide a conservative measure of the amount of glass reduction. Then this glass sample will be analyzed, by wet chemical methods, for the amount of reduced iron, and the total iron content of the glass [17]. If the feed is too reducing, modifications will be made to allow processing of the material, e.g. blending with material which is more oxidizing, or specification of lower feed rates for the overly reduced material.

A longer-term solution is to use a model of the reactions of the various species in the feed to optimize system operation for any batch. Thus, feeds which contain high levels of reducing agents may be run slower, or at higher temperatures, or with various cover gases in the melt plenum to optimize processing. An excellent example of such a model is the staged reaction approach of Morris, described elsewhere in these proceedings [18].

USE OF ARTIFICIAL INTELLIGENCE TECHNIQUES

The models described above are algorithmic in nature; i.e. they require quantitative inputs and produce quantitative outputs. However, much of the important information about how the process is operating is qualitative in nature. As an example, the DWPF melter is equipped with TV cameras which will monitor the melter at all times. The camera image will provide non-quantitative information, but this will often be the

best indication an operator has that certain problems are occurring, for example that the feed rate is too high.

Another problem in using only algorithmic models is that they do not easily take into account heuristic, or common-sense, information. As an example, if both the power to the melter pour spout and the glass flow rate are remaining constant, but the readings from a thermocouple in the pouring section are drifting up, common sense would indicate that the thermocouple is probably failing. But it would be difficult to reduce this to an algorithm.

For these reasons, SRL has begun to explore artificial intelligence technologies as adjuncts to purely algorithmic process controls. Although Edwards gives a more detailed discussion of a particular application elsewhere in these proceedings [19], it is worthwhile to briefly discuss some of the benefits we are finding in this technology.

Rapid Development and Deployment

The initial system developed by Edwards was set up in six man-months, and was immediately used. It would have taken 3 - 10 times more effort to adapt conventional control technology to this job, and to develop a system which could be deployed.

Flexibility

The system described by Edwards is highly modularized; whenever additional knowledge is developed about how the process works, it can be easily added without affecting the rest of the system. This is especially important for nuclear waste vitrification, because we do not have the decades of experience in melter operations that exist in the commercial glass industry. We expect that we will learn a great deal for several years after operation begins. When one operator observes a pattern of behavior which can be associated with a problem, this can be easily captured in the system, and is then not lost when the operator is not available for operation.

Completeness

One of the most important aspects of this technology is its ability to make use of all of the information about the process - both quantitative and qualitative. Thus, the system can perform heat balance calculations, and also can inform the operator if a component has gone out of service because of an interlock with some other piece of equipment.

CONCLUSION

The DWPF will make extensive use of models to ensure that the process and product are reliable. As we gain more experience in the melting process, and better information about glass composition-property relationships, these models will be updated to reflect this better understanding. Our goal is to have a control system which is effective immediately, and which can be improved in the future. Artificial intelligence techniques have shown great promise in allowing the control system to rapidly reflect the results of running the vitrification process, and are likely to be an important component in future control systems.

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Table I. Composition of glasses containing Savannah River Plant radioactive waste, in wt %.

Component	Initial Glass	High Fe Glass	High Al Glass
SiO_2	51.0	50.8	56.0
Na_2O	9.0	9.4	8.4
Fe_2O3	8.3	8.4	4.9
B_2O3	7.7	7.8	7.0
Al_2O3	4.7	2.8	6.9
Li_2O	4.5	4.5	4.8
FeO	3.7	3.8	2.2
K_2O	3.4	3.5	2.2
MnO	2.0	2.0	2.1
MgO	1.4	1.4	1.5
CaO	1.2	1.1	0.8
Other	3.1	4.5	3.3

Table II. Important process and product variables which must be controlled, and their control limits.

Variable	Limit(s)
Durability	Release < 1 $g/m^2 \cdot d$ on 28 day MCC-1 leach test; to ensure that repository can meet regulatory requirements
Viscosity	> 20 poise; to limit corrosion and volatility
	< 100 poise; to ensure reliable glass pouring and to achieve design basis glass production rate
Liquidus	< 1050°C; to prevent precipitation of crystalline phases in the melter
Glass redox	Fe^{2+}/Fe^{3+} < 0.35; to prevent Ni metal formation
	Fe^{2+}/Fe^{3+} > 0.05; to prevent foaming

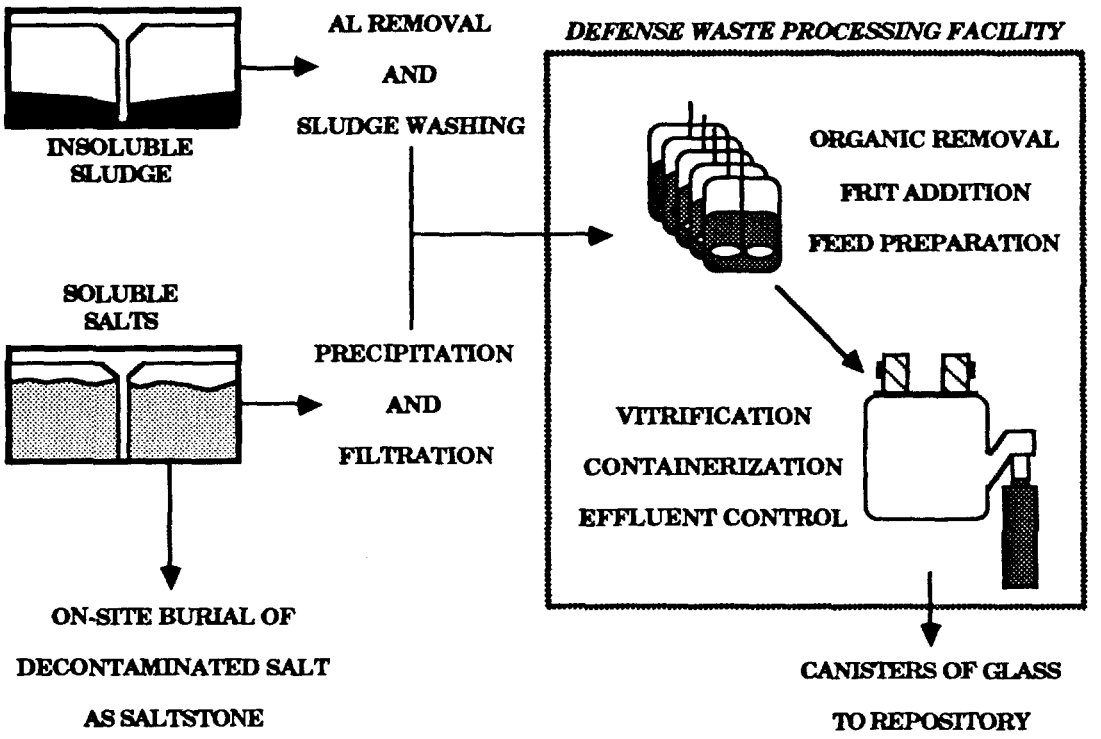

Figure 1. The Defense Waste Processing Facility vitrification process at the Savannah River Plant.

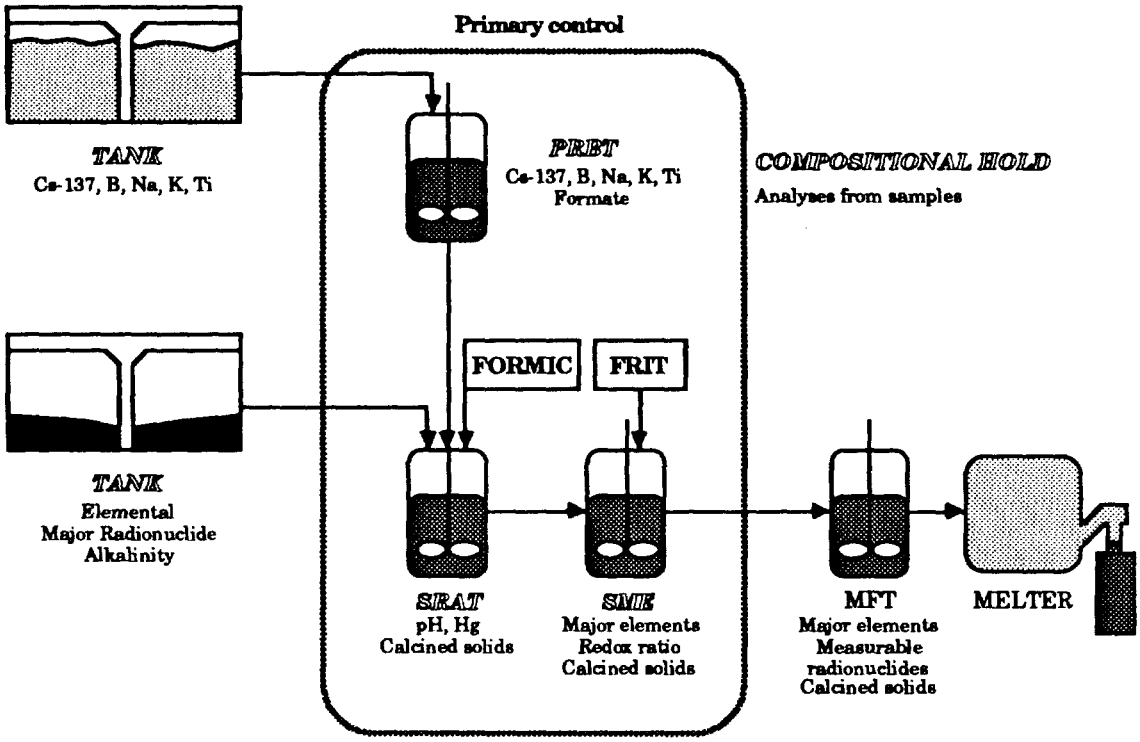

Figure 2. Control of glass composition in the DWPF process.