

A Novel Process Control System for a Glove Box Vitrification System

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ABSTRACT

The Nuclear Materials Technology (NMT) division at Los Alamos National Laboratory (LANL) is developing and demonstrating a glove box vitrification system. This system will treat evaporator bottoms (EVB) resulting from the management of effluents from the nitrate dissolution and recovery processes currently employed to purify plutonium (Pu²³⁹).

The vitrification system will be required to evaporate and dry the EVB, calcine the nitrate salts to oxide, and melt the waste constituents in conjunction with a glass frit. The final product will be a TRU borosilicate glass that meets all the acceptance criteria for disposal at the Waste Isolation Pilot Plant (WIPP) in southern New Mexico.

This paper will discuss the process control system (PCS) developed for the glove box vitrification system. The PCS is an Allen-Bradely PLC based system that controls the temperature of the melter, and uses a novel set of control parameters to produce the vitrified product.

INTRODUCTION

The primary processing components of the TA-55 Vitrification System are contained in a glove box to reduce the potential for radioactive contamination, and protect the workers from exposure to plutonium and nitric acid. The system components enclosed in the glove box include the melter, cooling jacket, and melt can handling mechanisms. Auxiliary components, such as the off-gas scrubber, scrub solution recycle tanks, scrub solution intermediate storage tanks, melter feed tanks, frit delivery system, associated pumps, heat exchangers and piping are located outside the glove box. The system is depicted in Fig. 1.

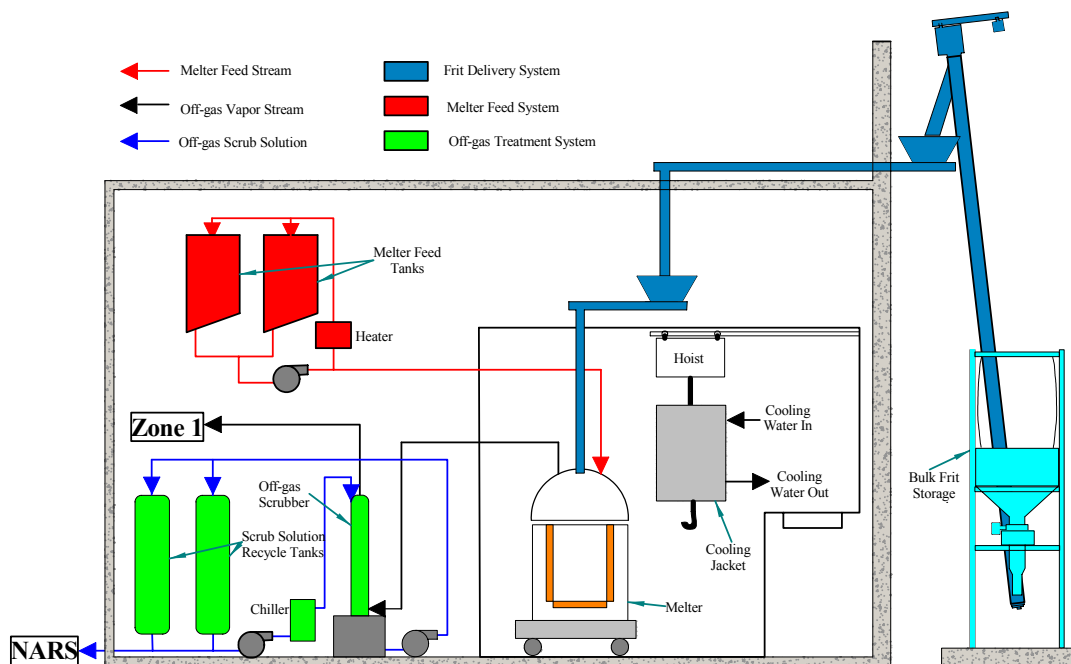


Fig. 1 TA-55 Vitrification System

The wastes to be processed in the vitrification system are generated during the dissolution, purification, and recovery of Pu oxide. This process generates approximately 40,000 L of effluents per year. The effluents are concentrated by evaporation, and generate around 2000 L of evaporator bottoms (EVB), and 38,000 L of distillate annually. The distillate is sent to the TA-55 Nitric Acid Recycle System (NARS). The NARS generates 14M nitric acid, which is sent back to the dissolution process. The EVB are currently sent to a cementation process, where they are stabilized for eventual disposal at WIPP. This process is shown in Fig. 2.

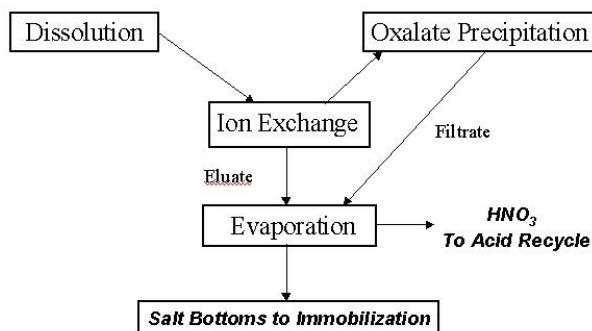


Fig. 2 Flowsheet for Nitric Acid Recovery of Plutonium

The EVB are composed of nitric acid and water, and are saturated with nitrate salts. The primary metals are Al, Ca, Fe, K, Mg and Na. The primary radionuclides are Pu and Am. The vitrification process has been designed to process the 2000 L of EVB generated annually in ten batches, each consisting of a nominal 200 L EVB and 125 kg of glass frit.

BACKGROUND

The development of the TA-55 Vitrification System began with the design of the primary system components and demonstration testing of the process flowsheet. The majority of these components are commercially available. The melter, off-gas scrubber, feed system, tanks, frit delivery system, and glove box have been fabricated and delivered. The primary components of the system have been set up in a non-radioactive facility for final demonstration and process optimization. This testing will be initiated later this fiscal year.

The process development work has been conducted using a non-radioactive bench scale system. This system is presented in Fig. 4, and has undergone over 1000 hours of testing to date. The primary focus of the test program has been the development of the process control system (PCS) and demonstration of acceptable processing conditions.

The primary system components and the bench scale system are presented in Fig. 3.



Fig. 3 Non-radioactive Test Systems

Processing Objectives

The process of vitrifying EVB consists of four primary physical conversions:

- Evaporate (nitric acid and water)
- Dry (remove waters of hydration)
- Calcine (convert nitrates to oxides)
- Melt

The development of acceptable processing conditions to accomplish these conversions evolved over the course of the bench-scale test program. Several key processing objectives were identified at the beginning of the development process, and have been used throughout the project to establish “acceptable” operation. They were:

- Contain waste materials in the melt can
 - minimize solids carry-over to the off-gas system
 - avoid bed expansion/foaming
- Process in a timely manner
- Generate a glass product that meets processing criteria
 - melts at < 1100°C
 - homogeneous

While seemingly obvious, these objectives have guided the development process through many different operating scenarios. Difficulty in achieving one or more of the objectives has resulted in the abandonment of several processing options and modification of equipment. More importantly, our understanding of the physical conversions that occur during processing evolved over the course of the development effort, generally as a result of not satisfying one of the objectives. This evolution of understanding, and the relationship to the processing objectives should become more apparent in later sections of this paper.

Early Experiences

Our initial attempts to treat EVB were based on the operation of Department of Energy (DOE) High Level Waste (HLW) vitrification systems; semi-continuous introduction of liquid waste onto a molten glass pool. This type of operation was abandoned due to the excessive entrainment of solids into the off-gas treatment system that resulted in significant contamination of the off-gas scrub solution. Several other processing scenarios were attempted, and the results are presented in Table I.

Table I Operational Experiences – Bench-scale Test System

Operation	Observations
Molten Glass Pool	Excessive splattering and entrainment of solids to off-gas system
Heated Frit Bed - single feed nozzle	Creation of "stalagmites". Poor distribution of waste oxides in the frit bed. Carry-over of solids to off-gas system
Heated Frit Bed - multiple feed nozzles	Poor distribution of solids in the frit bed. Waste oxide concentrated in upper layer of frit. Carry-over of solids to off-gas system
Flooded Frit Bed - continuous introduction of waste	Moderate splattering and entrainment of solids to off-gas system. Multiple processing steps and reduced throughput. Complex feed delivery system and difficult process control.

The initial processing scenarios were directed at completing the required conversions as quickly as possible in an attempt to maximize processing throughput. Limited processing space precluded the use of a separate calcination step, and previous experience at TA-55 has demonstrated the difficulty of evaporating and drying EVB in a batch mode¹. Concentrated nitric acid/nitrate salt solutions tend to foam excessively and the operation is difficult to control. The processing scenarios presented in Table I were attempted in an effort to avoid these difficulties and circumvent batch evaporation of EVB. Unfortunately, these attempts were unsuccessful for the reasons presented in the table. Excessive entrainment/carry-over of solids into the off-gas system nullified the effectiveness of these early processing scenarios. Crucible tests also showed that equal distribution of waste oxides in the frit bed was essential to effective melting².

Operation of system using a "batch mode" seemed to be the only avenue for achieving equal distribution of waste oxide in the frit bed and an acceptable final product. The question then became how to control EVB evaporation/concentration and prevent foaming, splattering, entrainment of solids plus achieve even distribution of waste oxide in the frit bed.

Process control of batch-continuous evaporation traditionally consists of a thermocouple measuring the temperature of the bulk solution and a feedback loop that adjusts the power to the heater accordingly. In our application, the melt can is loaded with glass frit/EVB and the system heated to the boiling point of the nitric acid/water/saturated salt solution (~120°C). The temperature is maintained until the solution was evaporated, then the temperature is increased to drive off the waters of hydration (~250°C), increased again to calcine the nitrate salts to oxide (~500°C), and finally the system is heated to the melt temperature of the mixed waste/frit oxide (~1050°C). The obvious initial attempt at process control for this operation was a simple temperature ramp with adequate hold times to accomplish the desired physical conversion.

The results of batch processing using this type of control were less than successful. The operation proceeded as expected until the concentration of the solution reached a point where excessive foaming was observed and the system had to be shut down. Carry-over of solids into the off-gas system was unacceptable and the system was unstable. It was also noted that the continuous introduction of waste solution to the system complicated the operation and control. Several attempts were made to adjust the temperature ramp rate and other traditional control parameters to prevent excessive conditions. Although this approach may have ultimately been successful, it became clear that traditional concepts for batch evaporation were not adequate and a new strategy was needed.

Local vs Bulk Conditions During Evaporation Sequence

Recognizing that the traditional control methods for batch evaporation were based on the bulk conditions of the system, the development team decided to re-visit the processing objectives and examine the physical conversions based on local conditions.

Heat is supplied to the system using resistance heaters. In the bench-scale unit, there is one, 6" heater providing 2200 watts radially, and a 400 watt bottom heater. The melt can is 5" schedule 10, 316-stainless steel pipe with a welded bottom, and is 8" high. The melt can is loaded with approximately 1/2 kg of frit and 2 L of surrogate EV. The system is monitored using Type K thermocouples (TCs) located between the melt can outer wall and the radial heater, in the frit bed at 1/4", 1/2", 1" from the inner wall of the melt can and in the center of the frit bed. There is also a TC located between the bottom heater and the bottom of the melt can (see Fig. 4).

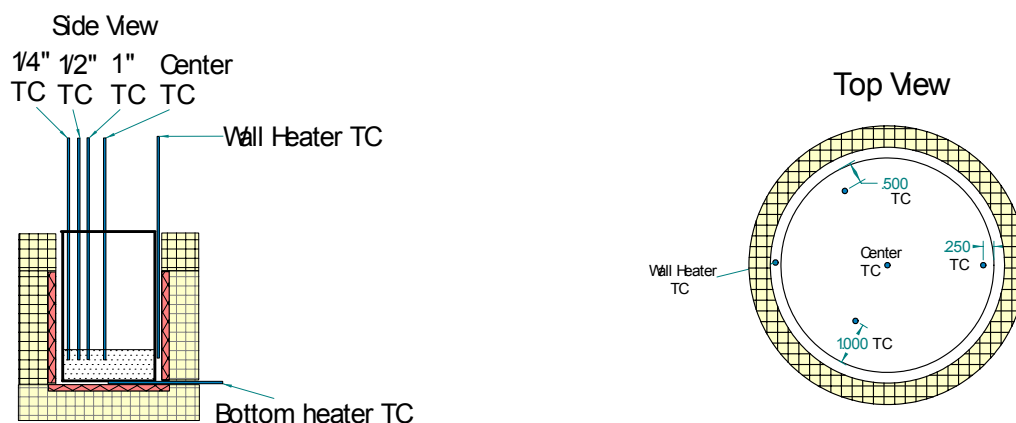


Fig. 4 Bench-scale Test Unit

The first choice for operation is to transfer heat through the metal container wall and into the EVB/frit mixture. The rate at which the solution boils at these surfaces (the boiling heat flux) is clearly a function of the wall ΔT (temperature difference between the melt can wall and the bed just inside the melt can wall). If the wall ΔT is too great, the nucleate boiling flux will

become high enough to result in rapid boiling and entrainment. Further increase in wall delta-T will result in film boiling and more severe entrainment.

This condition is especially detrimental if it occurs at the wall-liquid surface interface. Rapid boiling at the wall-liquid surface interface results in solution/solids being ejected into the head space and entrained to the off-gas system. Attempts to control the heat input through the melt can wall (wall delta-T control) resulted in test runs that were extremely time consuming and difficult to control. When the heat transfer rate from the wall heater to the melt can wall is faster than from the melt can wall into the bed, the result is a high delta-T. The wall heater responds to a high delta-T by reducing the power on the wall heater to a point of shutting off. This is because, the heater temperature stays high for a while after the heater power is reduced, causing the delta-T to continue to be high or perhaps even to increase, until the heat is absorbed into the bed and the wall cools down to below the target delta-T to bring the wall heater back up. This cycle is time consuming and hard to control due to the slow response times. It was also noted that rapid boiling at the wall-liquid surface interface sometimes resulted in foaming at the liquid surface and drying of the foam creating a dry hard cap of salts at the liquid surface. If this cap is formed, gases are likely to be formed under the cap and the cap can be pushed up and out of the can.

A second option is to put heat into the system using the bottom heater. This mode of operation has the disadvantage of reduced surface area when compared to heating through the melt can wall. The advantage, however, is that frit and EVB reside above the heat transfer surface and boiling occurs well below the solution surface. The resulting temperature increase causes boiling on the bottom surface of the melt can and also on the warmer solids in this region. Heat moves from the melt can surface and warmer solids into the adjacent liquid. More heat goes into the center of the can bottom than goes into the area near the outer edge of the bottom heater, resulting in a high temperature profile between the outer area and the center of the bed. This uneven heating through the can bottom results in the drying of the bed in the center, forming a dry column in the center with a hard dry salt forming on the outer side of the column, even before boiling is started at the outer area of the bed. Therefore the heat is transferred up this column and out of the system with very little heat transferred to the outer area of the bed. Attempts to raise the heat on the bottom heater to dry the outer area of the bed showed to be inefficient, and therefore; the use of the bottom heater exclusively to evaporate, dry and calcine was not acceptable.

Knowing that more heat goes into the center of the bed from the bottom heater and that more heat goes into the outer area of the bed from the wall heater, a third option was imposed to use both heaters. The bottom heater is used to put heat into the center of the bed and the wall heater to put heat into the outer area of the bed. This method results in a more consistent temperature profile across the bed. In normal operation, the primary control of the bottom heater is a bottom can temperature target, but the heater output is limited to a bed temperature rise rate target, and a wall/bed delta-T temperature target. The wall heater is set to control the dynamic wall/bed delta-T, and is limited by the same bed temperature rise rate target as the bottom heater during the evaporation stage. By using both heaters in this manner, we are able to concentrate the heat input into the lower portion of the frit bed and evaporate solution evenly from the bottom of the bed. This allows the cooler solution above the frit bed to fill the voids left from the evaporation and

the dry salts layer to form from the bottom up. Controlling the bed rise rate assures that we are evaporating in the frit bed; not from the surface of the solution where rapid surface boiling would cause loss of solution/salts to the off-gas system. It also avoids forming a dry salt layer on the surface of the frit bed, which would prevent the solution from filling the voids in the frit bed or could form a dry salt cap that can trap vapors generated during evaporation. This method of control has been shown to:

- increase the concentration of waste oxide in the frit bed,
- improve the distribution of oxides throughout the frit bed, and
- minimize the carryover of solution/salts to the off-gas system.

Additional Process Control Requirements

The previous sections have described the challenges and methods used to control the evaporation sequence of the vitrification process. The description has been focused on the essential parameters and has attempted to tie them to the physical phenomenon occurring during operation. There are, however, a significant number of additional requirements built into the process control logic. These additional control steps are referred to as control states. Obviously, there are additional control requirements included in the PCS for the remainder of the processing steps. The PCS for the vitrification system has been divided into five sequences:

- System Heat-up
- Evaporation
- Drying
- Calcination
- Melting

Within each control sequence there are a varying number of control states that are necessary for effective process control. The comprehensive list of control sequences and states is presented in Table II. The table identifies the control sequence and the control states that are required to complete the required physical conversion while meeting the established processing objectives. As stated earlier, the process control logic has evolved over many hours of development testing, and has resulted in a fairly complex PCS for the vitrification system. The success of the development effort can be attributed to a “linkage” between the physical events occurring during each conversion to a set of unconventional control parameters that have been established based on the local conditions in the frit/EVB/melt can system that drive that particular conversion. This approach has resulted in a PCS that differs markedly from conventional control logic.

Table II Process Sequences, Control States, and Heater Controls

Sequence	Control State	Bottom Heater	Wall Heater
Sequence 1 Heatup	1.10 Timed Heat-up	100 % ON	100 % ON
	1.20 Seq. 1 time > Heat-up minutes and control state = 1.1	OFF	OFF
	1.30 Control State = 1.20 and the Wall Temp. Rise Rate < 0.0 OR if Control State = 1.30	Bed Temp. Rise Rate is controlled to the Seq. 2 Bed Temp. Rise Rate Limit	Wall Temp. is controlled to the 1/4" Tc plus Seq. 1 Target Delta-T, or 110°C whichever is greater
	1.31 Bed Rise Rate is > Seq. 2 Rise Rate limit	Bed Temp. Rise Rate to the Seq. 2 Bed Temp. Rise Rate Limit	Bed Temp. Rise Rate to the Seq. 2 Bed Temp. Rise Rate Limit
	1.40 Low bed temp. > Seq. 1 Bed Temp Target, (Hold in Sequence)	Lowest bed Temp. to the Seq. 1 Bed Temp Target	Wall temp. to the Seq. 1 Bed Temp. Target minus 5
Sequence 2 Evaporation	2.10 Bottom can temp. > Seq. 2 wall/bottom temp. target minus 95 and the Wall/Bed Delta-T is < -5 OR if the Bottom can Temp. is greater then or equal to the Wall/Bottom Temp. Target	Bottom can Temp. to the Seq. 2 Wall/Bottom Temp. Target	Wall/bed Delta-T to the Seq. 2 Dynamic Delta-T Target
	2.11 Bed Temp. Rise Rate is > Seq. 2 Bed Temp. Rise Rate Limit	Bottom can Temp. to the Seq. 2 Wall/Bottom Temp. Target	Bed Temp. Rise Rate to the Seq. 2 Bed Temp. Rise Rate Limit
	2.20 Wall/Bed Delta-T is > -5 and the Bottom can Temp. is < the Wall/Bottom Temp. Target	Wall/Bed Delta-T to the Seq. 2 Dynamic Delta-T Target	OFF
	2.21 Bed Temp. Rise Rate is < 0.0	Bed Temp Rise Rate to a Bed Temp. Rise Rate of 0.0	OFF
	2.22 Bed Temp. Rise Rate is < 0.0 and the Bottom heater % output is > then 95%	Bed Temp Rise Rate to a Bed Temp. Rise Rate of 0.0	Bed Temp Rise Rate to a Bed Temp. Rise Rate of 0.0
	2.23 Wall/Bed Delta-T > Seq. 2 target Delta-T	Wall/Bed Delta-T to the Seq. 2 Dynamic Delta-T Target	OFF
	2.24 Wall/Bed Delta-T < Seq. 2 target Delta-T and the Bed Temp. Rise Rate > 0.0, Or the bottom heater % output < 95% and the Bed Temp. Rise Rate > 0.0	Wall/Bed Delta-T to the Seq. 2 Dynamic Delta-T Target	OFF
	2.25 Bed Temp. Rise Rate > Seq. 2 Bed Temp. Rise Rate Limit	Bed Temp Rise Rate to the Seq. 2 Bed Temp. Rise Rate Limit	OFF
	2.30 Lowest Bed Temp. > Seq. 2 Bed Temp. Target, OR if the control state is = 2.3 (Hold in Sequence)	Lowest Bed Temp. to the Seq. 2 Bed Temp. Target	Wall temp. to the Seq. 2 Bed Temp. Target minus 5
Sequence 3 Dry	3.10 Low Bed Temp. > Seq. 2 Bed Temp. Target	Bottom can Temp. to the Seq. 3 Dynamic Can Temp. Target	Bed Temp. Rise Rate to the Seq. 3 Bed Rise Rate Target
	3.20 Seq. 3 Dynamic Delta-T target < Wall/Bed Delta-T	Bottom can Temp. to the Seq. 3 Dynamic Can Temp. Target	Wall/Bed Delta-T to the Seq. 3 Dynamic Delta-T Target
	3.30 Low Bed Temp. > Seq. 3 Bed Temp. Target, Or if the control state is = 3.3 (Hold in Sequence)	Lowest Bed Temp. to the Seq. 3 Bed Temp. Target minus 2	Wall Temp. to the Seq. 3 Bed Temp. Target minus 5
Sequence 4 Calcine	4.10 Low Bed Temp. > Seq. 3 Bed Temp. Target	Bottom can Temp. to the Seq. 4 Dynamic Can Temp. Target	Bed Temp. Rise Rate to the Seq. 4 Bed Temp. Rise Rate Limit
	4.20 Wall/Bed Delta-T > Seq. 4 Dynamic Delta-T Target	Bottom can Temp. to the Seq. 4 Dynamic Can Temp. Target	Wall/Bed Delta-T to the Seq. 4 Dynamic Delta-T Target
	4.30 Lowest Bed Temp. is > the Seq. 4 Bed Temp. Target (Hold in Sequence)	Lowest bed Temp. to the Seq. 4 Bed Temp. Target Minus 5	Wall Temp. to the Seq. 4 Bed Temp. Target Minus 5
Sequence 5 Melt	5.10 Low Bed Temp. > Seq. 4 Bed Temp. Target	OFF	Wall Temp. Rise Rate to the Seq. 5 Rise Rate Target
	5.20 Wall Temp. > Wall/Bottom Temp. Target	OFF	Wall Temp. to the Seq. 5 Wall/Bed Temp. Target

CONCLUSIONS

The evaporation, drying, calcination, and melting of a TRU evaporator bottom waste stream has proven to be a complex process operation requiring the development and demonstration of a novel process control system. This system has evolved over the course of 1000+ hours of testing, and is based on a set of unconventional control parameters. These parameters were derived from a basic understanding of the physical processes occurring within the frit/evaporator bottom/melt can system. Using appropriate control parameters based on the physical conversion occurring within the system has resulted in a PCS that meets all the process objectives for the LANL vitrification system.

REFERENCES

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- 2 D. W. Mullins, R. K. Nakaoka, "Processing Techniques for Vitrification of TRU Evaporator Bottoms" Los Alamos National Laboratory report LA-UR-02-3786 (2002).