1 of 1

Conf-940815--89

PNL-SA-22937

MULTIPURPOSE OPTIMIZATION MODELS FOR HIGH LEVEL WASTE VITRIFICATION

M. Hoza

August 1994

Presented at the
Spectrum '94: International Nuclear and Hazardous Waste Management Conference
August 14-18, 1994
Atlanta, Georgia

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MULTIPURPOSE OPTIMIZATION MODELS FOR HIGH LEVEL WASTE VITRIFICATION

Mark Hoza
Pacific Northwest Laboratory[a]
P.O. Box 999
Richland, Washington 99352
(509) 375-6782

ABSTRACT

Optimal Waste Loading (OWL) models have been developed as multipurpose tools for high-level waste studies for the Tank Waste Remediation Program at Hanford. Using nonlinear programming techniques, these models maximize the waste loading of the vitrified waste and optimize the glass formers composition such that the glass produced has the appropriate properties within the melter, and the resultant vitrified waste form meets the requirements for disposal. The OWL models can be used for a single waste stream or for blended streams. The models can determine optimal continuous blends or optimal discrete blends of a number of different wastes. The OWL models have been used to identify the most restrictive constraints, to evaluate prospective waste pretreatment methods, to formulate and evaluate blending strategies, and to determine the impacts of variability in the wastes. The OWL models will be used to aid in the design of frits and maximize the waste fraction in the glass for High-Level Waste (HLW) vitrification.

I. INTRODUCTION

High-Level Waste at Hanford will be converted to a borosilicate glass for disposal. The glass will need to meet both processability and durability restrictions. The processability conditions will ensure that the glass has properties (viscosity, electrical conductivity, and liquidus temperature) within ranges known to be acceptable for the vitrification process. Durability restrictions will ensure that the resultant glass will meet quantitative criteria for disposal.

An experimental program, the Composition Variability Study (CVS), is developing property models which correlate physical properties to glass compositions and temperature history.[b] Linear and second order property models have been developed for viscosity, electrical conductivity, and durability. The property models are described in the above report. Bounds on property values, limits on the composition of individual components in the glass, and other restrictions are also found in the report.

The Optimal Waste Loading (OWL) models are being developed as a set of tools to aid the glass formulation processes. In the most basic implementation, the OWL model will calculate the maximum waste loading and an optimal frit composition such that all constraints on the glass (as identified in the CVS study) are satisfied. The current implementation of the OWL models can be used to identify limiting constraints, evaluate blending strategies, evaluate the effectiveness of pretreatment processes, and to explore the effects of property model uncertainty and vitrification process recycle on waste loading.

This paper describes the current OWL models and their uses. Section II states the general constrained optimization problem, while section III describes the general formulation of the OWL models. Section IV briefly discusses the implementation of the OWL models and Section V discusses the various OWL models and their uses. Section VI provides conclusions.

---

[a] Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

[b] Hrma, P.R. and G.F. Piepel. 1992. *Property/Composition Relationships for Hanford Waste Vitrification Plant Glasses -- Preliminary Results Through CVS-II Phase 2.* PHTD-92-03.01/K897, Pacific Northwest Laboratory, Richland, Washington.

II. THE GENERAL CONSTRAINED OPTIMIZATION PROBLEM

This section describes a general constrained optimization problem. In optimization problems, one wants to find the point x that produces the maximum (or minimum) value of some function f, and that meets a set of criteria called constraints. The problem would be stated as:

maximize $f(x)$

subject to $h(x) = 0$

$g(x) \leq 0$

where

- f is the objective function which we want to maximize (or minimize). It is a single (scalar) function of the unknown variables
- x is a vector $(x_1, x_2, \ldots, x_n)$ of the variables over which we optimize
- h is a vector function containing the equality constraints $(h_1(x), h_2(x), \ldots, h_p(x))$
- g is a vector function containing the inequality constraints $(g_1(x), g_2(x), \ldots, g_q(x))$

Each of the equality and inequality constraints is also a function of the unknowns. In general, the objective function and any or all constraints may be nonlinear.

III. FORMULATION OF THE BASE OWL MODEL

In this section the simple waste loading problem around which most of the OWL models are based is discussed. In this problem, frit (glass formers) is added to a single waste composition and the mass fraction of waste in the glass is maximized such that all the constraints are satisfied. The frit composition is varied as part of the optimization. The problem formulation is depicted graphically in Figure 1. The formulation of the problem is given below, while the objective function and the constraints are described in the next two sections. Specialized variations of this general problem are described in section V.

For the single mixture or single tank case, the optimization problem can be generally stated as follows:

<u>*Single Mixture Waste Loading Optimization Problem:*</u>

minimize *number of canisters*
or
maximize *waste loading per canister*

subject to *mass balance constraints*
CVS component bounds
multiple component constraints
solubility constraints
glass property constraints

The possible objective functions and each category of constraints will be discussed in turn in the next two sections.

A. Objective Function

The goal is to minimize the number of canisters of glass (number of glass logs) produced. The number of canisters can be expressed as total mass of waste oxides divided by the Total Mass of Waste oxides in the Glass (TMWG) per canister. (In keeping with convention, all compositions are expressed on an oxide basis, i.e. assuming all species are present as particular oxide forms. This convention is intended to assure a consistent calculational basis regardless of the actual chemical form of a component.) In the notation used throughout the OWL models, the objective is to

$$\text{minimize} \quad \frac{OxideMass}{TMWG}$$

Since the numerator is constant for a given problem, it is equivalent to maximize the amount of waste in each canister or the mass fraction of waste in each canister.

$$\text{maximize} \quad TMWG$$

or

$$\frac{TMWG}{MaxLogMass}$$

where MaxLogMass is a constant (1650 kg) which specifies the mass of a canister of glass. For the single mixture calculations the latter form for the objective function is used.

B. Reference Constraint Set

For the calculations described in this report, a single consistent set of constraints, based on the Phase II CVS study), was used throughout. This constraint set is referred to as the reference constraint set. *The reference constraint set should not be viewed as the final word on glass constraints. Ongoing or future experimental work may justify adding, modifying, or removing constraints*

from the reference constraint set. The constraints are discussed in the next several subsections.

1. Mass Balance Constraints

The mass balance constraints are equalities which define the relationships involved in the formation of glass from its components. The mass balance constraints for the waste + frit = glass (i.e. no recycle) case are presented. The extensions for the recycle case are straightforward, but are beyond the scope of this paper. As noted above, all masses are given on an oxide basis.

Define the mass of glass in a canister = Total Mass of Waste in the Glass + Total Mass of Frit in the Glass

$$MaxLogMass = TMWG + TMFG$$

Define the mass fraction of each component in the glass (FG) in terms of its mass fractions in the waste (FW) and the frit (FF), and the masses of waste and frit in the glass

$$FG_i = \frac{FW_i * TMWG + FF_i * TMFG}{MaxLogMass}$$

And finally, require that the mass fractions of all ten CVS components sum to one in the frit and in the glass.

$$\sum_{i=1}^{10} FF_i = 1.0$$

$$\sum_{i=1}^{10} FG_i = 1.0$$

2. CVS Component Bounds

These constraints limit the range of the mass fraction values each component can have in the calculated glass composition. They reflect the composition region over which the CVS was performed and define a hypercube in composition space which specifies the region over which the glass property models are considered valid. Compositions outside these limits will not necessarily produce unacceptable glasses. Rather, these compositions represent regions for which the glass property models must be extrapolated. Promising glasses outside these limits would have to be evaluated experimentally to determine their acceptability.

The upper and lower limits (UL, LL) used in the calculations are the bounds from phase 2a of CVS-II. These limits, and the CVS efforts on which they are based, reflect the early focus of glass design efforts on Neutralized Current Acid Waste (NCAW) waste. Ongoing and future experimental work may provide the basis for modifying these limits. For each of the ten CVS components, these constraints would be expressed as:

$$FG_{i,LL} \le FG_i \le FG_{i,UL}$$

The limits for each component are given in Table 1.

Table 1. CVS Component Bounds in Glass

Component	Lower Limit	Upper Limit
SiO_2	.42	.57
B_2O_3	.05	.20
Na_2O	.05	.20
Li_2O	.01	.07
CaO	.00	.10
MgO	.00	.08
Fe_2O_3	.02	.15
Al_2O_3	.00	.15
ZrO_2	.00	.13
Other[a]	.01	.10

(a) Other is a pseudo-component which represents all components in the waste other than the nine explicitly included.

3. Multiple Component Constraints

These constraints, formerly referred to as crystallinity constraints, also specify limits on the range of applicability of the glass property models. If the component bounds define the vertices of a hypercube in composition space, the multiple component constraints cut off some of the corners. These constraints earlier had served as rough substitutes for a liquidus temperature model, but it was found that these limits correlated poorly with occurrence of crystalline phases. The constraint names reflect their earlier purpose The constraints and the names by which they will be referred are given below:

Crystal1 $$\frac{FG_{SiO_2}}{FG_{Al_2O_3}} \ge 3.0$$

Crystal2 $FG_{MgO}+FG_{CaO}\leq 0.08$

Crystal3

$$FG_{Fe_2O_3}+FG_{Al_2O_3}+FG_{ZrO_2}+FG_{Other}\leq 0.225$$

Crystal4 $FG_{Al_2O_3}+FG_{ZrO_2}\leq 0.18$

Crystal5 $FG_{MgO}+FG_{CaO}+FG_{ZrO_2}\leq 0.18$

4. Solubility Constraints

These constraints limit the maximum value for the mass fraction of one or a combination of components (e.g. noble metals: Rh_2O_3 + PdO + Ru_2O_3). They are intended to represent solubility limits for the specified components. These limits cover species not included among the nine species covered in the CVS studies. (They are, of course, included within the tenth component "Other".) These limits are of the form

$$FG_k \leq FG_{k,UL}$$

Their limits are given in Table 2. As with all other constraints, they are subject to change if experimental studies demonstrate the need.

Table 2. Upper Limits on Mass Fractions of Solubility Components

Solubility Component, k	Upper Limit - $FG_{k,UL}$
Cr_2O_3	.005
F	.017
P_2O_5	.01
SO_3	.005
Noble Metals (Rh_2O_3 + PdO + Ru_2O_3)	.025

5. Glass Property Constraints

These constraints implement the glass property models developed in the CVS. The calculation of each property [viscosity, electrical conductivity, and durability (actually rate of release of boron) by either the Product Consistency Test (PCT) or Materials Characterization Center Test (MCC-1)] is of the form

$$\ln(MinVal) \leq \sum_{i=1}^{10} b_i FG_i + \sum_{i=1}^{10}\sum_{j\geq i} b_{ij} FG_i FG_j \leq \ln(MaxVal)$$

where b_i and b_{ij} are the coefficients of the first and second order terms respectively, and 10 is the number of components considered in the study. The limits on each of the constraints are given in the Table 3.

Table 3. Minimum and Maximum Glass Property Values

Property, units	MinVal	MaxVal
Viscosity, PaS	2	10
Electrical Conductivity, S/m	18	50
Durability (7-day release of boron by PCT), g/m^2	N/A	10
Durability (28-day release of boron by MCC), g/m^2	N/A	28

IV. IMPLEMENTATION OF THE OWL MODELS

The OWL models are implemented in the General Algebraic Modeling System (GAMS) (Brooke, et. al., 1992) and the optimization calculations are performed using MINOS 5.1 (Murtagh and Saunders, 1987) or CONOPT (Drud 1985). The models are implemented in a collection of modules. A specific model is built by specifying the modules to assembled. The various OWL models are described in the next section.

V. THE OWL MODELS AND THEIR USES

There are four core OWL models. They are described in the next section.

A. The OWL Models

The four OWL models are OWL-Base, OWL-Recyc, OWL-Uncert, and OWL-OptBlnd. These, combined with additional calculational modules, enable the performance of a wide range of calculations.

The OWL-Base model was described in Section III. It takes a single waste composition and combines it with frit of a variable composition to produce glass. Two variations of OWL-Base are used for blending calculations. The total blend calculation (Figure 2) combines the specified wastes to form a single blend.

That blended composition is the composition that is input to OWL-Base. In the discrete blend model, each waste goes to one blend; each blend contains one or more wastes (Figure 3). The model calculates all specified combinations of the specified wastes to form two or more blends. This is suitable only for small numbers of wastes to be blended.

OWL-Recyc adds a recycle stream to the waste and frit streams. The recycle stream calculation, which is based on a simplified HWVP flowsheet, is calculated as part of the optimization. It adds approximately 250 equations (constraints) and unknowns to the problem.

OWL-Uncert is a variation of OWL-Base that accounts for uncertainty in the physical property models.

OWL-OptBlnd calculates the optimal continuous blend for a set of wastes. In an optimal continuous blend, any fraction of any waste can go to any blend (Figure 4).

B. Uses of the OWL Models

The OWL models are being used for several purposes for a number of different projects.

1. Estimate Waste Loadings. Given a waste composition and total mass, the waste loading and mass of high-level glass produced can be calculated. Since there is a great deal of uncertainty in waste compositions, the calculated results should be considered estimates.

2. Examine the Effects of the Constraints. For each waste composition, a limiting constraint (one which prevents further increases in the waste loading) can be identified. If a single component limit is the limiting constraint, waste loadings could be increased if that component were removed by pretreatment.

3. Formulate Frit and Glass Compositions. For wastes limited by a single component bound, five of the six degrees of freedom (waste loading + five frit components) remain. By selectively tightening constraints, one can assure the glass will have the desired properties and operating headroom.

4. Examine the Effect of Property Model Uncertainty. The property models are empirically derived. The effect of the uncertainty in these models on the optimum waste loading can be examined.

5. Examine the Effect of Recycle. The effect of adding recycle to the waste and frit to form glass can be examined.

6. Formulate and Evaluate Blending Strategies. The use of blending as an option for reducing the volume of high-level waste glass required can be examined using total blend, discrete blending, and continuous blending calculations.

7. Evaluate Prospective Pretreatment Methods. Pretreatment flowsheets can be evaluated relative to the volume of glass the high-level portion of the waste would require.

8. Examine the Effects of Waste Variability. A crude assessment of the effects of variations in the waste composition can be made by varying, in turn, each of the components between their upper and lower bounds.

VI. CONCLUSIONS AND FUTURE WORK

The OWL models are proving to be a very useful tool in helping to understand the issues involved in the vitrification of high-level waste. Calculations using the models are being performed for a wide range of applications.

Work in progress will use mixed integer nonlinear programming methods to solve larger discrete blending problems and will develop techniques and models to better account for the uncertainty in waste compositions.

ACKNOWLEDGEMENTS

This work was sponsored by Westinghouse Hanford Company and the Department of Energy.

REFERENCES

Brooke, A., D. Kendrick, and A. Meeraus (1992). *GAMS User's Guide, Release 2.25*. The Scientific Press, San Francisco, California

Drud, A. (1985). *CONOPT--A GRG Code for Large Sparse Dynamic Nonlinear Optimization Problems*, Mathematical Programming, vol.31, 1985, page 153.

Murtagh, B. A., and M. A. Saunders (1987). *MINOS 5.1 User's Guide*, Report SOL 83-20R, December 1983, revised January 1987, Stanford University.

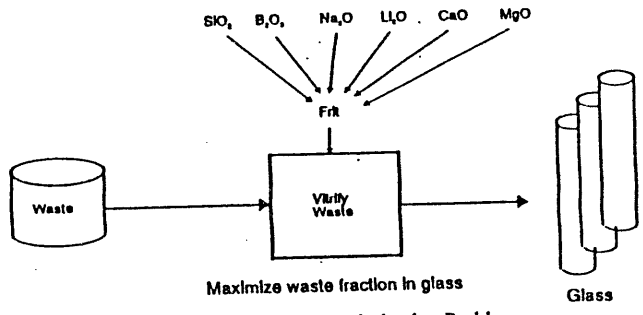

Figure 1. Simple Waste Optimization Problem

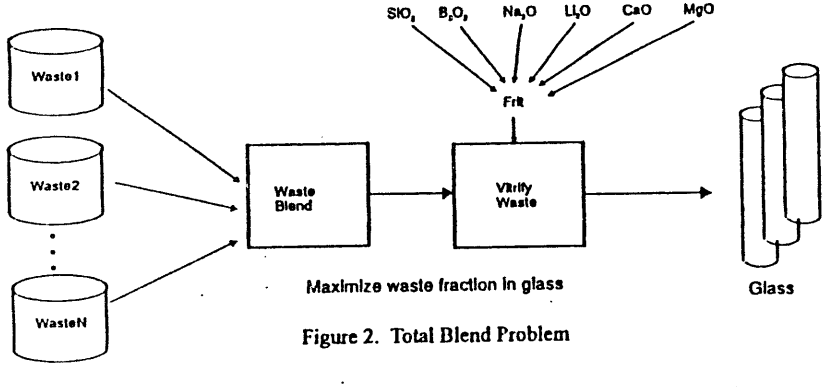

Figure 2. Total Blend Problem

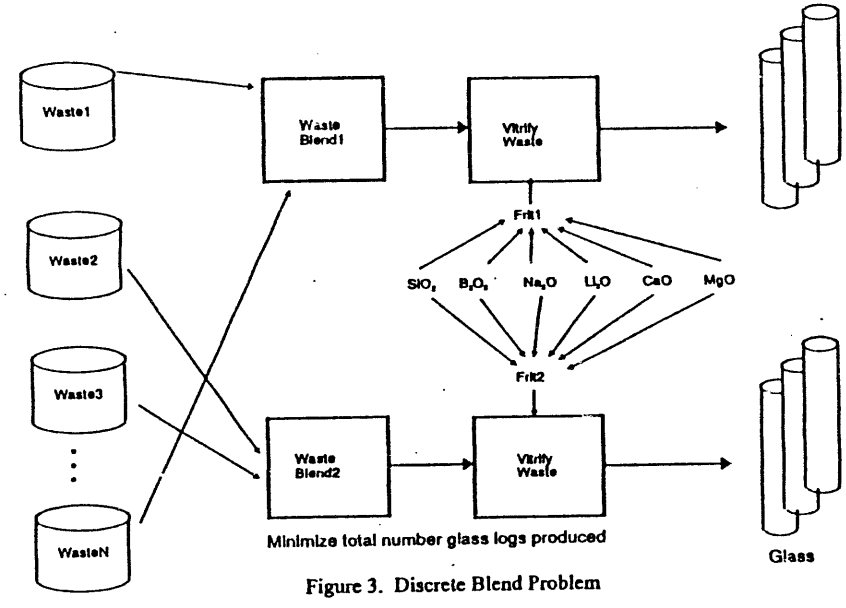

Figure 3. Discrete Blend Problem

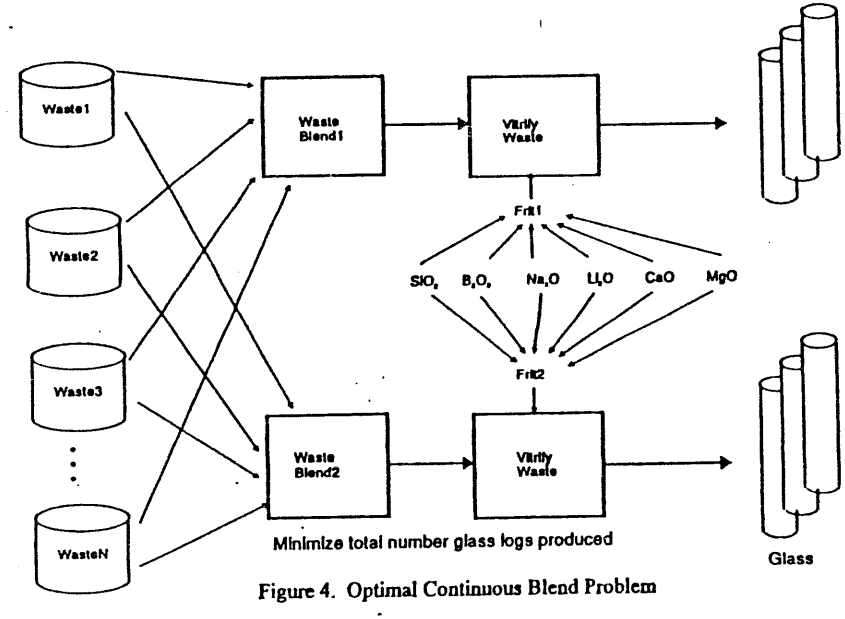

Figure 4. Optimal Continuous Blend Problem

AIIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

301/587-8202

Centimeter

Inches

MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

DATE
FILMED
12 / 14 / 94

END