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Thermal Analysis of Waste Glass Melter Feeds

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Office of River Protection

P.O. Box 450
Richland, Washington 99352

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THERMAL ANALYSIS OF WASTE GLASS MELTER FEEDS

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ABSTRACT

Melter feeds for high-level nuclear waste (HLW) typically contain a large number of constituents that evolve gas on heating. Multiple gas-evolving reactions are both successive and simultaneous, and include the release of chemically bonded water, reactions of nitrates with organics, and reactions of molten salts with solid silica. Consequently, when a sample of a HLW feed is subjected to thermogravimetric analysis (TGA), the rate of change of the sample mass reveals multiple overlapping peaks. In this study, a melter feed, formulated for a simulated high-alumina HLW to be vitrified in the Waste Treatment and Immobilization Plant, currently under construction at the Hanford Site in Washington State, USA, was subjected to TGA. In addition, a modified melter feed was prepared as an all-nitrate version of the baseline feed to test the effect of sucrose addition on the gas-evolving reactions. Activation energies for major reactions were determined using the Kissinger method. The ultimate aim of TGA studies is to obtain a kinetic model of the gas-evolving reactions for use in mathematical modeling of the cold cap as an element of the overall model of the waste-glass melter. In this study, we focused on computing the kinetic parameters of individual reactions without identifying their actual chemistry. The rough provisional model presented is based on the first-order kinetics.

I. INTRODUCTION

High-level waste (HLW) melter feeds typically contain a large number of constituents, such as oxides, acids, hydroxides, oxyhydrates, and ionic salts. On heating, while the feed is being converted to molten glass, multiple reactions occur, both successive and simultaneous. Most of these reactions evolve gas. Hydroxides, oxyhydrates, boric acid, and various crystalline forms release chemically bonded water, and reactions of nitrates with organics and molten salts (carbonates and nitrates) with solid silica release copious amounts of NO_x, CO_x, and O_2.[1-3] Consequently, the thermogravimetric analysis (TGA) of a HLW feed reveals multiple overlapping peaks.

As in our previous studies,[3-6] the melter feeds were formulated to produce a glass designed for vitrifying a high-alumina HLW. All-nitrate feeds were used to test the effects of sucrose additions at various carbon-nitrogen (C/N) ratios. The exothermic reaction of sucrose with nitrates helps the feed to melt faster in a continuous melter.[6]

Melter-feed gases make up 20 to 66% of the mass of glass, and their volume exceeds that of the glass by 10^3 to 10^4 times. This stream of gases escapes through the open pores and channels of the cold cap, a layer of reacting feed that rests on the melt surface in the glass melter. The ultimate aim of this study is to obtain a TGA-based kinetic model of the gas-evolving reactions for mathematical modeling

of a cold cap.[4] The model is a work in progress. Naturally, we first focused on obtaining the kinetic parameters of individual reactions without identifying their actual chemistry.

II. THEORY

Kissinger[8] derived the following formula for the activation energy, *B*, of gas-evolving reactions

$$B = -\frac{\mathrm{d}\ln(\Phi / T_m^2)}{\mathrm{d}(1/T_m)} \tag{1}$$

where Φ is the heating rate and T_m is the peak temperature.

For the first-order reaction, the reaction rate can be expressed as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A(1-x)\exp\left(-\frac{B}{T}\right) \tag{2}$$

where x is the fraction reacted, A is the pre-exponential factor, T is the temperature, and t is time. According to Kissinger,[8] A is given by the formula:

$$A = \frac{B\Phi}{T_m^2}\exp\left(\frac{B}{T_m}\right) \tag{3}$$

For multiple first-order reactions that are mutually independent, we can write:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \sum_i^N f_i A_i (1-x_i)\exp\left(-\frac{B_i}{T}\right) \tag{4}$$

where the subscript i denotes the reaction, f_i is the i^{th} reaction weight, and N is the number of major reactions.

III. EXPERIMENTAL

Table I displays the compositions of the melter feeds used. As described elsewhere,[5] these feeds were formulated to vitrify a high-alumina HLW to produce glass of the composition (with mass fractions in parentheses): SiO_2 (0.305), Al_2O_3 (0.240), B_2O_3 (0.152), Na_2O (0.096), CaO (0.061), Fe_2O_3 (0.059), Li_2O (0.036), Bi_2O_3 (0.011), P_2O_5 (0.011), F (0.007), Cr_2O_3 (0.005), PbO (0.004), NiO (0.004), ZrO_2 (0.004), SO_3 (0.002), K_2O (0.001), MgO (0.001), and ZnO (0.001). This glass was formulated for the Waste Treatment and Immobilization Plant, currently under construction at the Hanford Site in Washington State, USA. The baseline melter feed is labeled “A0.” A modified melter feed, A0-AN2,

was prepared as an all-nitrate feed to test the effect of sucrose addition on the gas-evolving reactions.[6] Sucrose was added to this feed at various C/N ratios from 0 to 1.25.

TABLE I. Melter Feed Compositions in g/kg glass

Component	A0	A0-AN2	Component	A0	A0-AN2
$Al(OH)_3$	367.50	367.49	Na_2SO_4	3.57	3.55
H_3BO_3	269.83	269.83	$Bi(OH)_3$	12.80	12.80
$Ca(NO_3)_2{\cdot}4H_2O$		210.56	Na_2CrO_4	11.13	11.13
CaO	60.80	10.79	KNO_3	3.03	3.04
$Fe(OH)_3$	73.83	73.82	$NiCO_3$	6.33	
$LiNO_3$		164.78	$Ni(NO_3)_2{\cdot}6H_2O$		15.58
Li_2CO_3	88.30		$Pb(NO_3)_2$	6.17	6.08
$Mg(OH)_2$	1.70	1.69	$Fe(H_2PO_2)_3$	12.43	12.42
$NaNO_3$		112.97	NaF	14.73	14.78
NaOH	99.53	46.30	$NaNO_2$	3.40	3.37
SiO_2	305.03	305.05	$C_2O_4Na_2$		1.26
$Zn(NO_3)_2{\cdot}4H_2O$	2.67	2.67	$Na_2C_2O_4{\cdot}3H_2O$	1.30	
$Zr(OH)_4{\cdot}0.654H_2O$	5.50	5.49	Total	1348.30	1655.43

Melter feeds were prepared, as described by Schweiger et al.[5], as slurries that were dried at 105°C overnight in an oven. For TGA, melter-feed samples of 10–60 mg were placed into a Pt crucible and heated from ambient temperature (~25°C) to 1200°C. The baseline feed, A0, was heated at the rates 1, 5, 10, 15, 20, and 50 K/min. The results were expressed in terms of the cumulative mass loss, x, and the rate of change, dx/dT or dx/dt. The T_m was either determined as a maximum on the dx/dT curve or estimated for shoulders on larger peaks.

IV. RESULTS

Figure 1 (left) shows the TGA curves for the A0 melter feed heated at several rates. As expected, the peaks shift to higher temperatures and the peak heights generally decrease as the rate of heating increases. The values of B and A, calculated with Eqs. (1) and (3), are listed in Table II. Also listed are values of f_is, obtained by fitting Eq. (4) to data via least-squares optimization; f_i represents the fraction of material reacted by i-th reaction. Figure 1 (right) compares the measured and calculated TGA curves for Φ = 10 K/min.

Figure 2 shows TGA curves for a series of AN2 melter feeds containing various additions of sucrose.

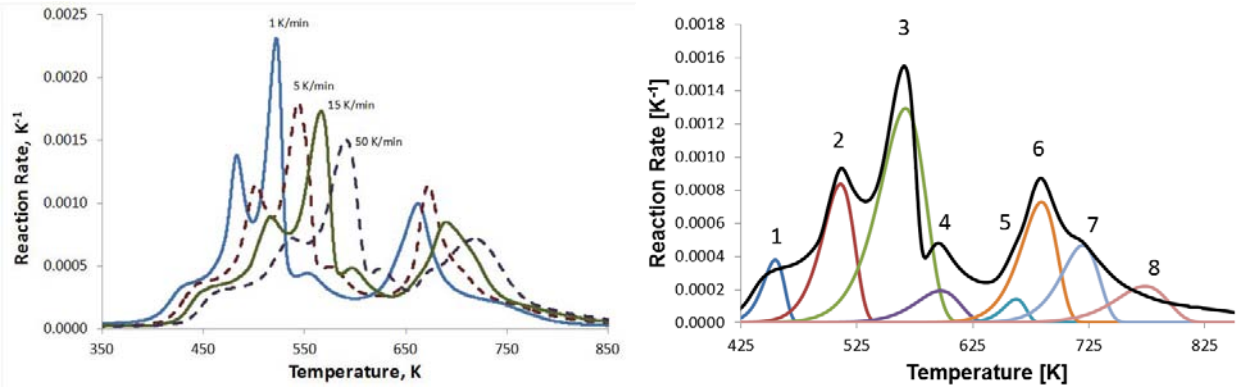

Fig. 1. TGA curves for A0 melter feed heated at various rates (left); measured and calculated curves are compared for melter feed heated at 10 K/min (right).

TABLE II. Kinetic Parameters for A0-Melter-Feed Reactions

Peak No.	T_m [K][(a)]	B [10^4 K]	A [s^{-1}][(a)]	f_i[(a)]
Peak 1	454	2.245	5.22E+19	0.009
Peak 2	511	1.875	1.06E+14	0.030
Peak 3	567	1.611	1.85E+10	0.066
Peak 4	597	1.834	1.89E+11	0.010
Peak 5	662	4.489	4.75E+27	0.004
Peak 6	684	2.985	9.57E+16	0.030
Peak 7	720	3.166	1.32E+17	0.020
Peak 8	773	2.601	2.97E+12	0.013
(a) Values were evaluated for Φ = 10 K/min.				

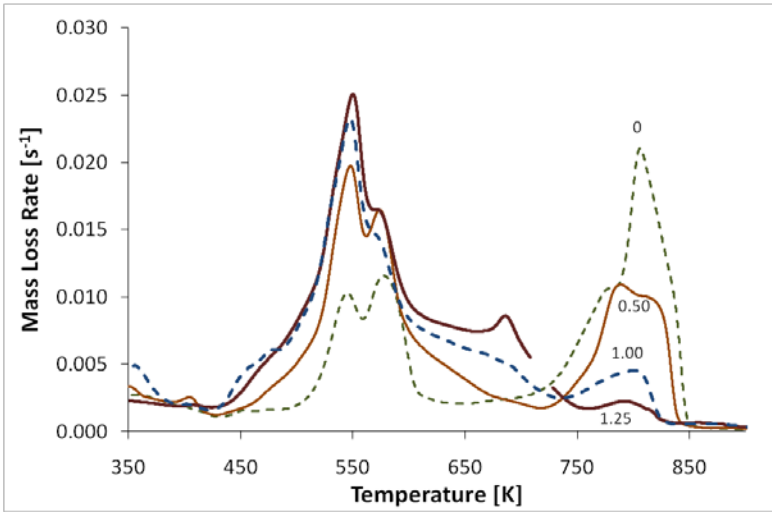

Fig. 2. TGA curves for A0-AN2 melter feeds with various additions of sucrose marked as C/N values (Φ = 5 K/min).

V. DISCUSSION

The goal of this study is to obtain an approximation of the reaction kinetics to be used for mathematical modeling of the cold cap as an element of the overall model of the waste-glass melter. Melter feed moves through the cold cap at a changing velocity while being exposed to a changing, not necessarily linear, temperature field to which the individual reactions respond according to their kinetics.[7] TGA data help the mathematical model of the cold cap to locate the sources of the escaping gas. To this end, reaction kinetics should be expressed in terms of differential equations. Hence, the aim of this study is to represent the reaction kinetics by a differential equation, such as Eq. (4). Accordingly, the success of the mathematical representation of the TGA data is defined by the goodness of fit between measured and calculated TGA curves regardless of the actual reaction mechanisms. As Fig. 1 (right) reveals, the agreement between measured and calculated TGA curves is only marginally satisfactory. There are several reasons for the lack of fit:

1. The mechanisms of melter feed reactions are complex and vary from peak to peak. The first-order reaction employed in this study is obviously not the best approximation for fitting the shape of each peak. The next step for achieving a better fit will be to assume that the reactions are n^{th} order, where n is a fitting parameter.
2. Reactions 1, 5, 7, and 8 appear as shoulders on peaks of reactions 2 and 6. This causes uncertainty in estimating T_m as a function of Φ. The estimates were improved by subtracting major peaks from the measured TGA curve.
3. Each reaction ideally has single values of B, A, f_i, and n, even though subsequent reactions may be affected by preceding reactions. This effect changes with the rate of heating. As Φ increases, slow reactions become less complete and new reactions may occur. For example, Reaction 5 is clearly identifiable only at Φ = 50 k/min.

As indicated by the TGA results obtained for feeds that vary in their C/N ratio (Fig. 2), sucrose addition caused nitrates to be destroyed early during melting while the temperature interval within which the residual nitrates evolve was not affected. The exothermic reaction of sucrose with nitrates occurred between 200 and 350°C (475 and 625 K). Similar, though smaller, peaks, which appeared even when no sucrose was added, were at least partly caused by the reaction of nitrates with the oxalate, an organic component of the waste (Table 1).

The irregular peaks that occurred in the temperature range of 450 to 575°C (725 to 850 K) were caused by the reaction of the liquid mixture of various nitrates with silicate and borate solids and melts. As the addition of sucrose increased, the heights of these peaks decreased. With increasing C/N, the double peak turned to a single one that did not disappear even at C/N = 1.25, indicating that somewhat higher C/N would be necessary to destroy all nitrates. A possibility exists of reducing multivalent oxides within the porous section of the cold cap by adding more reducing agents than needed for nitrate destruction. This would decrease the extent of foaming caused by oxygen evolving from redox reactions at temperatures above 900°C.

VI. CONCLUSIONS

The aim of this study, performed with feeds for vitrifying a high-alumina HLW, was to obtain an approximation of the kinetics of batch melting reactions regardless of their actual mechanisms. The main results are:

1. The TGA allows activation energies to be obtained for major melter-feed reactions. However, the determination of the reaction orders and the mechanisms of more complex reactions, such as reactions involving the glass phase, is a task for future effort.
2. Adding sucrose shifts the gas release to lower temperatures by destroying nitrates.

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