



Application of evolved gas analysis to cold-cap reactions of melter feeds for nuclear waste vitrification



Carmen P. Rodriguez^a, Jaehun Chun^{a,*}, Michael J. Schweiger^a, Albert A. Kruger^b, Pavel Hрма^{a,c}

^a Pacific Northwest National Laboratory, 902 Battelle Blvd., P.O. Box 999, MSIN K6-24, Richland, WA 99352, USA

^b U.S. Department of Energy Office of River Protection, Richland, WA 99352, USA

^c Division of Advanced Nuclear Engineering, Pohang University of Science and Technology, Pohang, Republic of Korea

ARTICLE INFO

Article history:

Received 20 August 2013

Received in revised form 20 June 2014

Accepted 23 June 2014

Available online 25 June 2014

Keywords:

Cold-cap reactions

Evolved gas analysis

Nuclear waste vitrification

Kinetic models

ABSTRACT

In the vitrification of nuclear wastes, the melter feed (a mixture of nuclear waste and glass-forming and modifying additives) experiences multiple gas-evolving reactions in an electrical glass-melting furnace. We employed the thermogravimetry-gas chromatography-mass spectrometry (TGA-GC-MS) combination to perform evolved gas analysis (EGA). Along with identifying the gases evolved, we performed quantitative analysis relating the weighted sum of intensities of individual gases in linear proportion with the differential thermogravimetry. The proportionality coefficients were obtained by three methods based on the stoichiometry, least squares, and calibration. The linearity was shown to be a good first-order approximation, in spite of the complicated overlapping reactions.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The cold cap is a floating layer of melter feed, or glass batch, on a pool of molten glass in a continuous electrical glass-melting furnace, termed a melter. For vitrifying nuclear waste glass [1–3], the feed, a mixture of waste with glass-forming and -modifying additives, is charged onto the cold cap that covers 90–100% of the melt surface. As the feed moves through the cold cap, it undergoes chemical reactions and phase transitions, through which it is converted to molten glass that moves from the cold cap into the melt pool.

The nuclear waste (i.e., mixed hazardous waste) contains 40–60 elements forming water-soluble salts, amorphous gels, and crystalline minerals. The conversion to glass proceeds over a wide range of temperatures (~100–1100 °C) spanning the formation of molten salts that react with feed solids, turning them into intermediate products and ultimately the glass-forming melt. Various cold-cap reactions evolve gases that escape from the cold cap through open pores. A small fraction of residual gases can be trapped in the glass-forming melt and cause foaming. Foam reduces the heat transfer from the molten glass into the cold cap, decreasing the rate of melting. Understanding the cold-cap reactions over the temperature range of the conversion process

helps formulate melter feeds for higher production rates, and hence an enhanced efficiency of the vitrification facility, by minimizing the overlap between the gas-evolving reactions and the formation of a highly viscous continuous glass-forming melt.

Gas-evolving cold-cap reactions release chemically bonded water and produce NO_x, O₂, and CO_x from reactions of nitrates with organics and reactions of nitrates, nitrites and carbonates with solids [4–17]. Pokorný et al. [3] modeled the kinetics of the gas-evolving cold-cap reactions using data from non-isothermal thermogravimetric analysis (TGA). Their model described the overall reaction rate as a sum of mutually independent *n*th-order reaction kinetics with the Arrhenius rate coefficients. For simplification, they neglected interactions between consecutive reactions and the complex responses of multicomponent molten salts and other reactants. Chun et al. [18] used a similar approach to develop a kinetic model for heat-consuming cold-cap reactions from simultaneous differential scanning calorimetry (DSC)-TGA data. It should be noted that reaction peaks identified in both approaches could result from the combination of sub-reactions in a similar temperature range unless the mixtures are treated at a wide range of heating rates.

The TGA- and DSC-based kinetic models provide phenomenological descriptions of the cold-cap reactions. Given the complexity of nuclear waste feeds and glass batches in general, these methods do not identify chemical species involved. Neither does the evolved gas analysis (EGA), but it does at least allow the

* Corresponding author. Tel.: +1 509 372 6257; fax: +1 509 372 5997.

E-mail address: jaehun.chun@pnnl.gov (J. Chun).

gases evolved to be recognized. Previous informative, yet semi-quantitative, EGA studies [19,20] analyzed off-gases from a laboratory-scale furnace without attempting to determine contributions of each of the gases to the mass losses. In this study, we correlate the mass loss rate from TGA with the well-resolved fluxes of gases as detected by gas chromatography–mass spectrometry (GC–MS) to obtain a quantitative EGA. The resulting model provides contributions of individual gases to mass losses associated with the feed-to-glass conversion.

The following section defines the basic concepts and relationships. Sections 3 and 4 describe the experiments and the results. Section 5 discusses the performance and applicability of the model as well as the prospective deeper characterization of feed melting reactions. In addition, the correspondence between the crucible experiments and the large-scale melting process from the viewpoint of sample preparation is examined.

2. Background for modeling

Assuming that the mass loss of the batch is only associated with gas evolution reactions [3], the change of the TGA sample mass equals the sum of mass changes of gases evolved. Thus,

$$-\frac{dm}{dt} = \sum_{j=1}^{N_g} \frac{dm_j}{dt} \quad (1)$$

where m is the sample mass, m_j is the j th off-gas mass, N_g is the number of gas species, and t is time. This assumption is reasonable for alkali-borosilicate batches for temperatures $< \sim 800^\circ\text{C}$; above this temperature, volatilization losses become appreciable.

For analysis with GC–MS, the flux of the j th gas species, represented via intensity, I_j , is proportional to the flux of molecular ions (or instrumentally produced current). Thus, $dm_j(t)/dt = F_j I_j(t')$, where F_j is the j th off-gas proportionality coefficient and $t' = t - \Delta t$; Δt is the time lag between the TGA signal and the MS detector reading due to the off-gas transfer to the MS detector. The dimension of F_j is such that the $F_j I_j$ product, which defines the j th gas production rate, has an appropriate [mass/time] unit. Eq. (1) then becomes:

$$-\frac{dm(t)}{dt} = \sum_{j=1}^{N_g} F_j I_j(t') \quad (2)$$

Provided that F_j and Δt are constant on the temperature interval of gas evolution, Eq. (2) can be integrated, obtaining:

$$\Delta m = \sum_{j=1}^{N_g} F_j \int_0^{t_f} I_j(t') dt \quad (3)$$

where Δm is the total mass loss measured by the TGA instrument and t_f is the time at which the gas evolution was complete (i.e., the time where the mass of the final glass can be defined via the remaining sample mass). The F_j coefficients can be obtained by fitting Eq. (2) to TGA-EGA data (see Section 4).

Generally, various factors need to be considered for a correlation between TGA and MS signals, such as flow patterns in the TGA chamber and carrier gas flow rates [21,22]. Eq. (2) (and thus Eq. (3)) would not be applicable in the presence of interfering experimental artifacts and/or a strong coupling of the reaction evolving the j th off-gas with other reactions (e.g., the gas consumed by other reactions). However, the implementation of the GC column (i.e., the affinity of gas species to a stationary phase inside the GC column) and the small volume of the GC injector may sufficiently reduce the broadening of the MS peaks to allow Eq. (2) to be a reasonable approximation (see Section 3.2 and Fig. 2).

The integral form of Eq. (1) can be written as:

$$\Delta m = \sum_{j=1}^{N_g} \Delta m_j \quad (4)$$

where Δm_j is the mass loss due to the j th off-gas. Comparing Eq. (3) with Eq. (4), we obtain:

$$F_j = \frac{\Delta m_j}{\int_0^{t_f} I_j(t') dt} \quad (5)$$

The mass fraction of the j th gas that evolved per unit mass of dry feed is defined as:

$$w_{F,j} = \frac{\Delta m_j}{m} \quad (6)$$

Note that $w_{F,j}$ was marked as w_j in [3]. The total gas-to-dry feed mass fraction is:

$$w_F = \sum_{j=1}^{N_g} w_{F,j} = \frac{\Delta m}{m} \quad (7)$$

Combining Eqs. (5) and (6), we obtain:

$$w_{F,j} = \frac{F_j}{m} \int_0^{t_f} I_j(t') dt \quad (8)$$

Assuming that the intensity response only depends on the nature of the gas, Eqs. (3), (5), and (8) are valid with identical values of F_j and Δt for any set of gas evolving reactions that are complete within the given interval of temperatures provided that the same instrument and experimental conditions are applied. Consequently, it is possible to calibrate the instrument for individual gases using solid samples that release a single gas in a single reaction. Then,

$$\Delta m_j = C_j \int_0^{t_f} I_j dt \quad (9)$$

where C_j is the j th gas calibration coefficient [23]. It follows from Eqs. (5) and (9) that $F_j = C_j$ for $j = 1, \dots, N_g$. To obtain a reliable calibration coefficient, three samples of a simple solid substance are typically analyzed to minimize experimental errors.

Table 1
Melter feed composition for high-alumina high-level waste in g kg^{-1} glass.

Chemicals	Mass (g)
Al(OH) ₃	367.50
H ₃ BO ₃	269.83
CaO	60.80
Fe(OH) ₃	73.83
Li ₂ CO ₃	88.30
Mg(OH) ₂	1.70
NaOH	99.53
SiO ₂	305.03
Zn(NO ₃) ₂ ·4H ₂ O	2.67
Zr(OH) ₄ ·0.654H ₂ O	5.50
Na ₂ SO ₄	3.57
Bi(OH) ₃	12.80
Na ₂ CrO ₄	11.13
KNO ₃	3.03
NiCO ₃	6.33
Pb(NO ₃) ₂	6.17
Fe(H ₂ PO ₄) ₃	12.43
NaF	14.73
NaNO ₂	3.40
Na ₂ C ₂ O ₄ ·3H ₂ O	1.30
Total	1349.6

Download English Version:

<https://daneshyari.com/en/article/673148>

Download Persian Version:

<https://daneshyari.com/article/673148>

[Daneshyari.com](https://daneshyari.com)