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

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A B S T R A C T

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.

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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 NOx, O2, and CO2 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 nth-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

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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,

\[ \frac{dm}{dt} = \sum_{j=1}^{N_g} \Delta m_j \]

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 \( t' = t - \Delta t \); \( \Delta t \) 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:

\[ \frac{dm(t)}{dt} = \sum_{j=1}^{N_g} F_j I_j(t') \]  

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

\[ \Delta m = \sum_{j=1}^{N_g} F_j \int_0^{t'} I_j(t') \, dt \]  

where \( \Delta m \) is the total mass loss measured by the TGA instrument and \( t' \) is the time at which the gas evolution was complete (i.e., the time when 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:

\[ \Delta m = \sum_{j=1}^{N_g} \Delta m_j \]  

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

\[ F_j = \frac{\Delta m_j}{\int_0^{t'} I_j(t') \, dt} \]  

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

\[ w_{Fj} = \frac{\Delta m_j}{m} \]  

Note that \( w_{Fj} \) was marked as \( w_j \) in [3]. The total gas-to-dry feed mass fraction is:

\[ w_F = \sum_{j=1}^{N_g} w_{Fj} = \frac{\Delta m}{m} \]  

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

\[ w_{Fj} = \frac{F_j \int_0^{t'} I_j(t') \, dt}{m} \]  

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 \( \Delta t \) 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,

\[ \Delta m_j = C_j \int_0^{t'} I_j(t') \, dt \]  

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

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)₃</td>
<td>367.50</td>
</tr>
<tr>
<td>H₂BO₃</td>
<td>269.83</td>
</tr>
<tr>
<td>CaO</td>
<td>60.80</td>
</tr>
<tr>
<td>Fe(OH)₃</td>
<td>73.83</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>88.30</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>1.70</td>
</tr>
<tr>
<td>NaOH</td>
<td>99.53</td>
</tr>
<tr>
<td>SiO₂</td>
<td>305.03</td>
</tr>
<tr>
<td>Zn(NO₃)₂·4H₂O</td>
<td>2.67</td>
</tr>
<tr>
<td>Zr(OH)₄·0.65H₂O</td>
<td>5.50</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>3.57</td>
</tr>
<tr>
<td>Bi(OH)₃</td>
<td>12.80</td>
</tr>
<tr>
<td>Na₂CrO₄</td>
<td>11.13</td>
</tr>
<tr>
<td>KNO₃</td>
<td>3.03</td>
</tr>
<tr>
<td>NiO</td>
<td>6.33</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
<td>6.17</td>
</tr>
<tr>
<td>Fe(H₂PO₄)₂·5H₂O</td>
<td>12.43</td>
</tr>
<tr>
<td>NaF</td>
<td>14.73</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>3.40</td>
</tr>
<tr>
<td>Na₂CO₃·3H₂O</td>
<td>1.30</td>
</tr>
<tr>
<td>Total</td>
<td>1349.6</td>
</tr>
</tbody>
</table>

Table 1: Melter feed composition for high-alumina high-level waste in g kg⁻¹ glass.
3. Experimental

3.1. Feed materials

Table 1 shows the melt feed composition used in this study. As described previously [3,8,24], this feed, denoted as A0, was formulated to vitrify a high-alumina high-level waste to produce glass of the following composition (mass fractions in parentheses): SiO₂ (0.305), Al₂O₃ (0.240), B₂O₃ (0.152), Na₂O (0.096), CaO (0.061), Fe₂O₃ (0.059), Li₂O (0.036), Bi₂O₃ (0.011), P₂O₅ (0.011), K₂O (0.007), Cr₂O₃ (0.005), PbO (0.004), NiO (0.004), ZrO₂ (0.004), SO₂ (0.002), K₂O (0.001), MgO (0.001), and ZnO (0.001). This glass was designed for the Hanford Tank Waste Treatment and Immobilization Plant, currently under construction at the Hanford Site in Washington State [25]. As described by Schweiger et al. [24], the simulated melt feed was prepared in the form of slurry that was dried, crushed into powder, and placed in an oven at ~105°C overnight. As discussed in Section 3.3, the slurry feed was used, instead of the direct mixing and melting batched chemicals, to simulate the actual melt feed as closely as practicable, even though subsequent drying and storing operation produce secondary effects of exchange of gases with the atmosphere. As shown below, EGA made it possible to discern these effects.

3.2. TGA-GC–MS system

In the study, we used a simultaneous TGA-GC–MS coupled system consisting of a NETZSCH STA 449 F1 Jupiter®. Simultaneous TGA-DSC instrument simultaneously coupled to an Agilent 7890A gas chromatograph equipped with an Agilent 5975C single quadrupole mass spectrometer. Evolved gases moved directly from the TGA chamber using helium as a carrier gas (under atmospheric pressure) to the GC–MS via heated transfer tubing. Evolved gases flowed through the GC sampling loop, and, in every minute, a partitioned segment was injected into the GC column, eluted with helium gas, and the gases were speciated by the GC before they entered the MS detector for analysis. Unlike a conventional capillary coupling, the stationary phase in the GC, along with a small injection volume, provided different interactions with each gas in the mixture, allowing a better resolution (i.e., avoiding significant broadening of the peaks in the MS).

The TGA instrument temperature and sensitivity were calibrated, following the manufacturer guidelines. To check for leaks, impurities, and residues from TGA/GC and peripheral setups (e.g., pumps and valves), multiple ‘blank’ runs without a sample were performed at the heating rate of 10 K min⁻¹ from 50°C to 1200°C.

The EGA was begun by placing 61.7 mg of the sample, prepared following the procedure in Section 3.1, into a platinum crucible. After loading the crucible into the TGA furnace, the instrument was stabilized, following manufacturer guidelines, by flowing helium through the system a couple of times. Simultaneously, to reduce background noises, the GC–MS instrument was stabilized by flowing helium through the system for 2–3 h and then run for about 10 min. As the open crucible with the sample was heated at 10 K min⁻¹ from 50°C up to 1200°C, helium was used as both a purge gas (at a constant flow rate of 20 ml min⁻¹) and protective gas (at a constant flow rate of 40 ml min⁻¹). The GC injector was set to splitless mode. The GS-CarbonPLOT capillary column, specifically designed for low molecular weight gas molecules, such as N₂, CH₄, CO₂, N₂O, and H₂O, was 30 m long and 320 μm in inner diameter and possessed a 3-μm film thickness. The GC–MS instrument ran under a helium atmosphere with a constant column flow rate of 1.5 ml min⁻¹. To avoid possible condensation, the valve box (containing a 250 μl sampling loop), the transfer tubing, and the GC column were held at a high enough temperature (>100°C). The reproducibility was checked at the optimized setting conditions (i.e., temperature, size of crucible, and flow rates specified) multiple times. Data were collected from TGA and GC–MS at the intervals of ~0.5 min and ~1 min, respectively.

The National Institute of Standards and Technology (NIST) mass spectral database [26], containing a collection of electron ionization mass spectra for various molecular species, was employed to identify evolved gases. For the MS, ionization energy was set to 20 eV, the scan range m/z (mass-to-charge ratio) was 10–100, and the GC–MS interface was set to 280°C.

4. Results

Fig. 1 shows the normalized mass loss (TG), its time derivative (DTG), and intensity from GC–MS. The four gases, CO₂, H₂O, NO, and O₂, were identified by matching observed m/z patterns in MS with the NIST spectroscopy library database. Fig. 1(b) displays the intensity in arbitrary units obtained as the MS signal multiplied by 10⁻⁶, which is applied for all results in our study. Note that it determines the order of magnitude of F_j (and C_j) because the F_j (and C_j) product should provide the same jth gas production in rate, irrespective of such normalization. As shown in Fig. 1(b), the major gases are CO₂ and H₂O with significant overlapping. The minor NO peak and the tiny O₂ peak coincide with the major peak of CO₂ while H₂O continues to evolve. The first DTG peak seen in Fig. 1(a) at ~10 min (~150°C) did not occur in the DTG results reported in our previous study [3]. We attributed this peak to the release of excess water accumulated in the sample by adsorption (also reported by Krämer [17]) and capillary condensation of atmospheric moisture.

To match the DTG and GC–MS temperature scales, data were smoothed with spline interpolation and a 1.5-min time lag was applied. The time lag of the off-gas transfer from TGA to MS detector corresponds to the 1.5 ml min⁻¹ flow rate through the transfer line and the 30-m GC column with 320-μm inner diameter.

![Fig. 1](image-url)
 provided that no jth gas was evolved from, or received by, the sample during feed preparation and storage. This method can be applied to feed constituents that are sufficiently stable, such as nitrates and nitrites, evolving NO and O₂. However, as expected, bonded water was partially liberated during feed preparation and some water and CO₂ were taken up from the atmosphere during dry feed storage, though simultaneous loss of water by slow room-temperature reactions cannot be ruled out.

The least squares method is based on fitting Eq. (2) to DTG and EGA data using least squares regression. This method is limited to gas-evolving reactions that are independent and do not have coincident peaks. As Fig. 1(b) indicates, this is not the case for the NO and O₂ peaks, which are eclipsed by the CO₂ peak. Finally, the calibration method uses a solid subjected to a single gas-evolving reaction in order to obtain the C_j coefficients (by Eq. (4)) as the F_j s. This method should work for all gases but needs to be checked with the other two methods.

The following subsections describe the application of the three methods to experimental data. The common source of uncertainty is that the small size of the sample containing a large number of components can cause composition deviations.

4.1. Stoichiometry method

The amounts of gases that evolve from the batch chemicals (listed in Table 1) during the vitrification process can be obtained based on the stoichiometry of batch reactions involved in the conversion of the batch chemicals and minerals (Table 1) to molten glass (Section 3.1). The mass loss associated with this process is the result of the release of the volatile components, such as H₂O and CO₂, to the atmosphere. Thus, the mass fraction of the jth gas evolved from the original batch per unit mass of glass is defined as the mass of the jth gas, (Δm_j), released from the chemicals batched per the mass of glass produced (m_G):

\[
\omega_{bj} = \frac{\Delta m_j}{m_G}
\]

Clearly, \(m_G = m_B - \Delta m_{th}\), where \(m_B\) is the total mass of chemicals batched to make glass (listed in Table 1) and \(\Delta m_{th}\) is the total mass of all gases evolved, \(\Delta m_B = \sum_{j=1}^{N_c} \Delta m_{bj}\). The subscript B stands for batched chemicals. Based on the batched composition listed in Table 1, stoichiometric calculation allows us to obtain the following \(\omega_{bj}\) values: \(\omega_{BSTO}=0.0558\), \(\omega_{BNO}=0.0041\), \(\omega_{BNO}=0.0023\), and \(\omega_{BNO}=0.2871\). The summation of these values is the total mass loss from batched chemical per glass \(\omega_B=0.3493\).

Generally, considering the sample preparation mentioned in Section 3.1, \(\omega_{bj}\) consists of three contributions: the fraction released or acquired during sample preparation (\(\omega_{jp}\)), the fraction released or acquired during sample storage (\(\omega_{js}\)), and the fraction released during conversion reactions (\(\omega_{jh}\)):

\[
\omega_{bj} = \omega_{jp} + \omega_{js} + \omega_{jh}
\]

Thus, the actual mass loss from dry feed per unit mass of glass (as measured by the EGA of the dry feed sample), \(\omega_G = \sum_{j=1}^{N_c} \omega_{jh}\), is lower than \(\omega_B\) unless \(\omega_{jp} = \omega_{js} = 0\) for all gases. Since \(\omega_G = \Delta m/m_G\), we obtain \(\omega_G = \omega_B/(1 - \omega_B) = 0.2751\), which is indeed significantly lower than \(\omega_B\).

As stated above, \(\omega_{js}\) for NO and O₂ can be safely estimated based on the stoichiometry of the batch chemicals because these gases are neither released to nor absorbed from the atmosphere during sample preparation. Hence, for \(j = NO\) and O₂, \(\omega_{jp} = \omega_{js} = 0\) and

![Fig. 2. Gas evolution rates for gaseous species by TGA and GC-MS with the proportionality coefficients from three different methods: (a) stoichiometry method, (b) least squares method, and (c) calibration method.](image-url)
Table 2
Proportionality coefficients of H₂O and CO₂ gas evolved per unit mass of dry feed, and calculated total gas-to-dry feed mass fraction based on three methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>F_{H₂O}</th>
<th>F_{CO₂}</th>
<th>w_{F,CO₂}</th>
<th>w_F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometry</td>
<td>1.280</td>
<td>0.099</td>
<td>0.0437</td>
<td>0.2751</td>
</tr>
<tr>
<td>Least squares</td>
<td>1.150</td>
<td>0.136</td>
<td>0.0603</td>
<td>0.2748</td>
</tr>
<tr>
<td>Calibration</td>
<td>1.140</td>
<td>0.131</td>
<td>0.0590</td>
<td>0.2701</td>
</tr>
</tbody>
</table>

thus \( w_{F,j} = w_{F,b} \). Since \( w_{F,j} = w_{F,b} / (1 + w_C) \), we obtain \( w_{F,NO} = 0.0032 \), and \( w_{F,O_2} = 0.0018 \).

As mentioned, not all bonded water from the batched chemicals is retained in the dry feed. Some originally bonded water was liberated during feed preparation, especially drying, due to water-releasing chemical reactions. Also, some water was acquired from the atmosphere during dry feed storage or slowly lost by continuing reactions. Hence, \( w_{F,j,NO} \) and \( w_{F,j,O_2} \) can be substantial.

Assuming, for simplicity, that the difference between \( w_F \) and \( w_I \) is solely attributed to \( H₂O \) and the only sources of \( CO₂ \) in the sample are the oxalate and carbonates from the batch, we obtain \( w_{F,CO₂} = 0.0437 \). The difference between \( w_F \) and the sum of the \( w_{F,j} \) values for \( NO, O_2, \) and \( CO₂ \) then equals \( w_F - w_{F,CO₂} \).

By Eq. \( (8) \), \( F_j = \frac{m_{w_j}}{\int_0^t f_j(t) \, dt} \). Performing the numerical integration and using the \( w_{F,j} \) values shown above, we obtain the stoichiometry-based values \( F_{NO} = 0.297 \) and \( F_{O_2} = 0.0693 \); the \( F_j \) values for \( H₂O \) and \( CO₂ \) are listed in Table 2.

Fig. 2(a) displays the evolution rates of individual gases as well as the sum of all gases, which is compared with the mass loss rate by the TGA. The EGA and TGA curves nearly coincide at \( t < \sim 30 \) min, indicating that the \( F_{H₂O} \) coefficient has an acceptable value. A substantial lack of fit for the peak to which \( CO₂ \) is a dominant contributor indicates that the \( CO₂ \) fraction in the sample was higher than that which came from the batch chemicals. The most likely cause was \( CO₂ \) absorption from the atmosphere by the highly alkaline feed.

4.2. Least squares method

The underestimated \( F_{CO₂} \) coefficient poses a question regarding the assumption that batch chemicals were the only sources of \( CO₂ \) in the sample. However, without this assumption, it is impossible to obtain \( F_{CO₂} \) for \( H₂O \) and \( CO₂ \) independently based on stoichiometry. Alternatively, \( F_{H₂O} \) and \( F_{CO₂} \) coefficients can be obtained by using the least squares analysis while leaving \( F_{NO} \) and \( F_{O_2} \) from the stoichiometry method unchanged. The analysis minimizes the value of the expression

\[
\sum_{i=1}^{n} \left[ \frac{dm(t)}{dt} \sum_{j=1}^{n} w_j \int_0^t f_j(t') \, dt' \right]^2
\]

where \( n \) is the number of GC–MS data measured (typically less than that from TGA — see Section 3.2 for time intervals of data collection). The optimized values of the \( F_{H₂O} \) and \( F_{CO₂} \) coefficients are listed in Table 2, showing that the fitted \( F_{CO₂} \) value is higher than that obtained based on the feed stoichiometry. As Fig. 2(b) demonstrates, the EGA and TGA curves based on the coefficients by the least squares method nearly coincide.

4.3. Calibration method

Additionally, a calibration based on single solid substances producing \( H₂O \) and \( CO₂ \), i.e., giving coefficients \( C_{H₂O} \) and \( C_{CO₂} \), can approximate the \( F_{H₂O} \) and \( F_{CO₂} \) coefficients. Fig. 3 displays the TGA-GC–MS analysis for a CaCO₃ sample (evolving \( CO₂ \) by the reaction \( CaCO₃ \rightarrow CaO + CO₂ \) heated at 10 K min⁻¹. The value \( C_{CO₂} = 0.131 \) was obtained by averaging from samples with 15.4 and 20.7 mg. Similarly, for calcium oxalate monohydrate (\( CaC₂O₄·H₂O \rightarrow CaC₂O₄ + H₂O \)) with 3.0, 4.8, and 9.3 mg samples, \( C_{H₂O} = 1.140 \) was obtained. These coefficients are compared in Table 2 with the coefficients based on stoichiometry (assuming zero external source of \( CO₂, NO, \) and \( O₂ \)) and the least squares analysis (assuming zero external sources or sinks of \( NO \) and \( O₂ \)).

Fig. 2(c) shows the comparison between DTG and EGA curves using the calibration method. Similar to the least squares method, the discrepancy between the EGA and TGA is minimal even in the

<table>
<thead>
<tr>
<th>Gas Loss Rate vs. Gas Evolution Rate</th>
<th>Least Squares</th>
<th>Calibration</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Loss Rate, mg min⁻¹</td>
<td>Leaest Squares</td>
<td>Calibration</td>
<td>Stoichiometry</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

This table shows the instantaneous mass loss rate versus gas evolution rate estimated by the stoichiometry, least squares, and calibration methods; the line represents identity.
major overlapping range (i.e., 30–50 min). Also, as the last column in Table 2 indicates, the difference in the total mass evolved relative to the TGA was insignificant.

Fig. 4 provides an additional evaluation of the proportionality assumption in terms of the instantaneous mass change rate by DTG versus the gas evolution rate by EGA showing that these rates nearly coincide except for values around sharp major peaks where EGA data were not detected (note that the EGA lines in Fig. 2 connect data points spaced ~1 min apart – see Section 3.2).

5. Discussion

5.1. Coefficient invariance

The results summarized in Table 2 imply that the following assumptions are likely to be valid:

a) \( f_j \) coefficients are virtually independent of temperature.

b) \( f_j \) coefficients are independent of the gas source.

c) The time lag, \( \Delta t \), is virtually constant over the gas-evolution temperature interval.

The near-match of DTG and EGA peak shapes and positions are consequences of these propositions, in addition to the minimization of experimental artifacts, such as the condensation of evolved gases and impurities from TGA/GC and peripheral setups. Thus, Eq. (2) is suitable as a first-order approximation. The proportionality assumptions stated, though based on a limited amount of data, may help optimize formulation of feeds for nuclear waste vitrification.

5.2. Identification of batch reactions

The previously reported TGA analysis [3] was solely focused on reaction kinetics. Identifying the gases by EGA provides a step toward the identification of the gas-evolving reactions for individual TGA peaks with the ultimate goal of understanding the reaction mechanisms; however, this can only be accomplished using different analytical tools. As Fig. 1 shows, the TGA peaks for individual gases overlap. By EGA results, the TGA peaks below 400 °C mainly correspond to \( \text{H}_2\text{O} \) evolution and the TGA peaks above 400 °C correspond to \( \text{CO}_2 \) evolution while \( \text{H}_2\text{O} \) is still evolving.

The missing information is the identification of the reactants and the products. While the EGA can add the chemical characteristics to the peaks identified in the TGA, it cannot differentiate between individual reactions that produce the same gas. An exact number of \( \text{H}_2\text{O} \)-evolving reactions would be also more than the number of peaks in Fig. 1. Based on the feed composition in Table 1, \( \text{H}_2\text{O} \) is released from hydroxides, acids, and hydrates, such as \( \text{NaOH}, \text{H}_2\text{BO}_3, \text{Al(OH)}_3, \text{Fe(OH)}_3, \text{Zn(NO}_3)_2, \text{4H}_2\text{O}, \text{Zr(OH)}_4, \text{0.654H}_2\text{O}, \text{Na}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}, \text{and Bi(OH)}_3 \). \( \text{NaOH} \) is likely to react with more acidic feed chemicals, such as \( \text{H}_2\text{BO}_3 \) and \( \text{Al(OH)}_3 \), in the slurry (pH ~11–12) [27,28]. Similarly, the TGA peaks above 400 °C are associated with reactions of carbonates, such as \( \text{Li}_2\text{CO}_3, \text{NiCO}_3 \), and \( \text{Na}_2\text{C}_2\text{O}_4 \) that may partly turn to \( \text{Na}_2\text{CO}_3 \) on heating.

Performing TGA and EGA for combinations of selected feed components, as Wilburn and Thomasson [4–7] have done for commercial glass batches, can indicate possible reactions in batches with a small number of well-defined components. X-ray diffraction can provide limited data about crystalline solids; however, as most of the feed solids form amorphous gels in the early stages of conversion, a host of methods is needed for understanding the conversion process for even a simplified melt feed [28].

5.3. Connection to vitrification of nuclear wastes in large-scale melters

Whereas the form of chemicals used to make glass have little impact on rock properties, experimental studies focused on vitrification technology require careful preparation of melter feeds to replicate as closely as possible the conversion process occurring in melters. However, exactly replicating the history of the nuclear waste since its creation, including decades-long aging in some cases, is neither possible nor necessary. Slurry-feed preparation described by Schweiger et al. [24] is deemed sufficient.

In U.S. vitrification plants, the slurry feed is directly charged into the melter, where it is transformed to molten glass. For experiments conducted with laboratory crucibles, the slurry is instead dried before the heat treatments. In addition to avoiding boiling in the laboratory furnaces, drying also eliminates capillarity-driven migration of water-soluble salts through the wet feed to the top surface of the sample, which would lead to undesirable non-uniformity in composition.

As demonstrated in this study, the discontinuity in the temperature history caused by drying the slurry and storing the feed at room temperature before further heat treatment can lead to an exchange of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) between the atmosphere and the dry samples, thus affecting the conversion process during the initial stages of melting. Using freshly prepared feeds and drying samples before heat treatment would eliminate this problem.

6. Conclusions

An understanding of the cold-cap reactions, although still incomplete, has been enhanced by the quantitative EGA via the TGA-GC–MS combination. The peaks identified by thermal analysis and represented by the kinetic model can thus be assigned to the evolving gases. Three different methods, based on stoichiometry, least squares, and calibration, gave rise to a linear relationship that correlates the overall mass loss rate from TGA with the sum of the production rates of individual gases from EGA. Future work could include identifying cold-cap reactions, including the reactants and the products.

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