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Thermal Analysis of Waste Glass Melter Feed

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

Office of River Protection

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THERMAL ANALYSIS OF WASTE GLASS MELTER FEED

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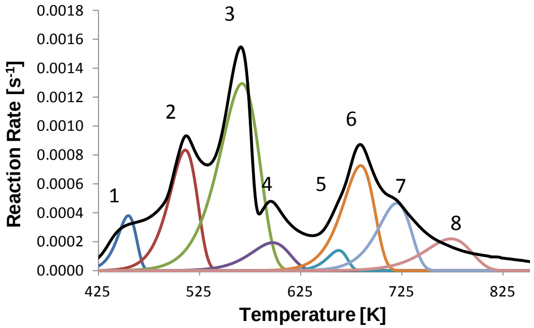
High-level waste melter feed

- **High-level waste (HLW) melter feed** contains oxides (SiO_2), acids (H_3BO_3), hydroxides ($Fe(OH)_3$), oxyhydrates ($AlO(OH)$), and ionic salts ($NaNO_3$).
- On heating, the feed is **converted to molten glass**.
- Conversion reactions **evolve gas**: H_2O, NO_x, CO_x, and O_2.
- 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.

Thermogravimetric analysis



- **The thermogravimetric analysis (TGA)** of a HLW feed shows **multiple overlapping peaks**.
- TGA has been performed for a **high-alumina HLW**.
- All-nitrate feeds were made 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).

Melter Feed Compositions in g/kg glass

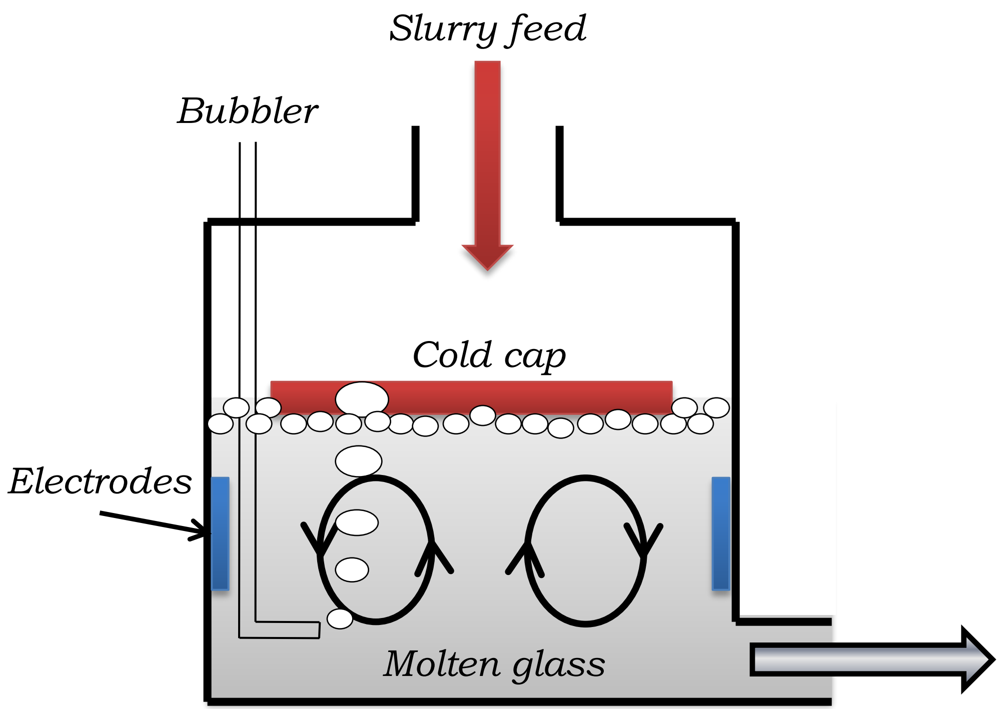
Component	Feed		Component	Feed	
	Base	All-nitrate		Base	All-nitrate
$Al(OH)_3$	367.50	367.49	Na_2SO_4	3.57	3.55
H_3BO_3	269.83	269.83	$Bi(OH)_3$	12.80	12.80
$Ca(NO_3)_2\cdot4H_2O$		210.56	Na_2CrO_4	11.13	11.13
CaO	60.80	10.79	KNO_3	3.03	3.04
$Fe(OH)_3$	73.83	73.82	$NiCO_3$	6.33	
$LiNO_3$		164.78	$Ni(NO_3)_2\cdot6H_2O$		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
$Zn(NO_3)_2\cdot4H_2O$	2.67	2.67	$Na_2C_2O_4\cdot3H_2O$	1.30	
$Zr(OH)_4\cdot0.654H_2O$	5.50	5.49	Total	1348.3	1655.43

Objective

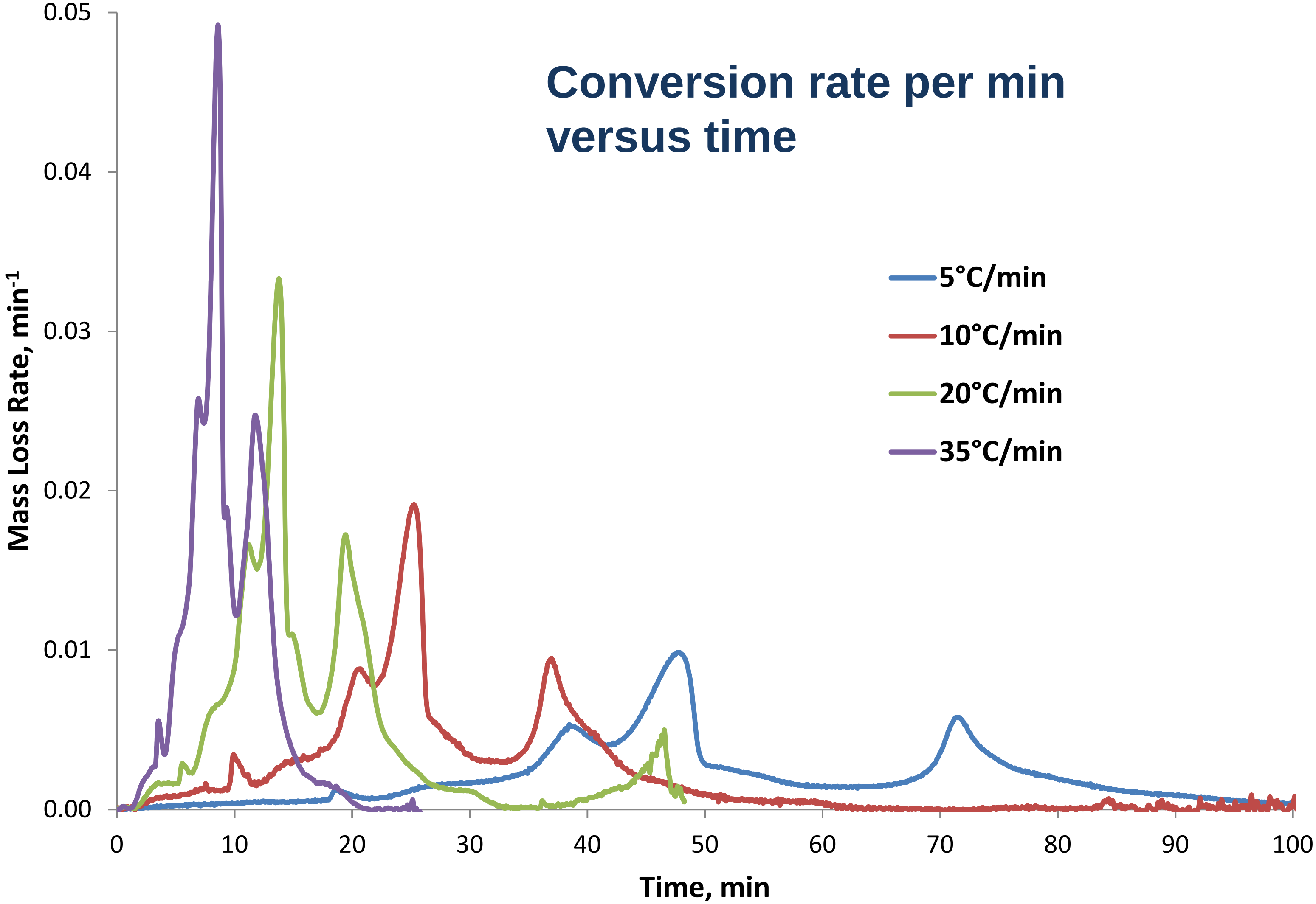
- The ultimate aim of this study is to obtain a TGA-based **kinetic model of the gas-evolving reactions** for mathematical modeling of a cold cap.
- We focus on obtaining the **kinetic parameters** of individual reactions without identifying their actual chemistry.

Cold cap

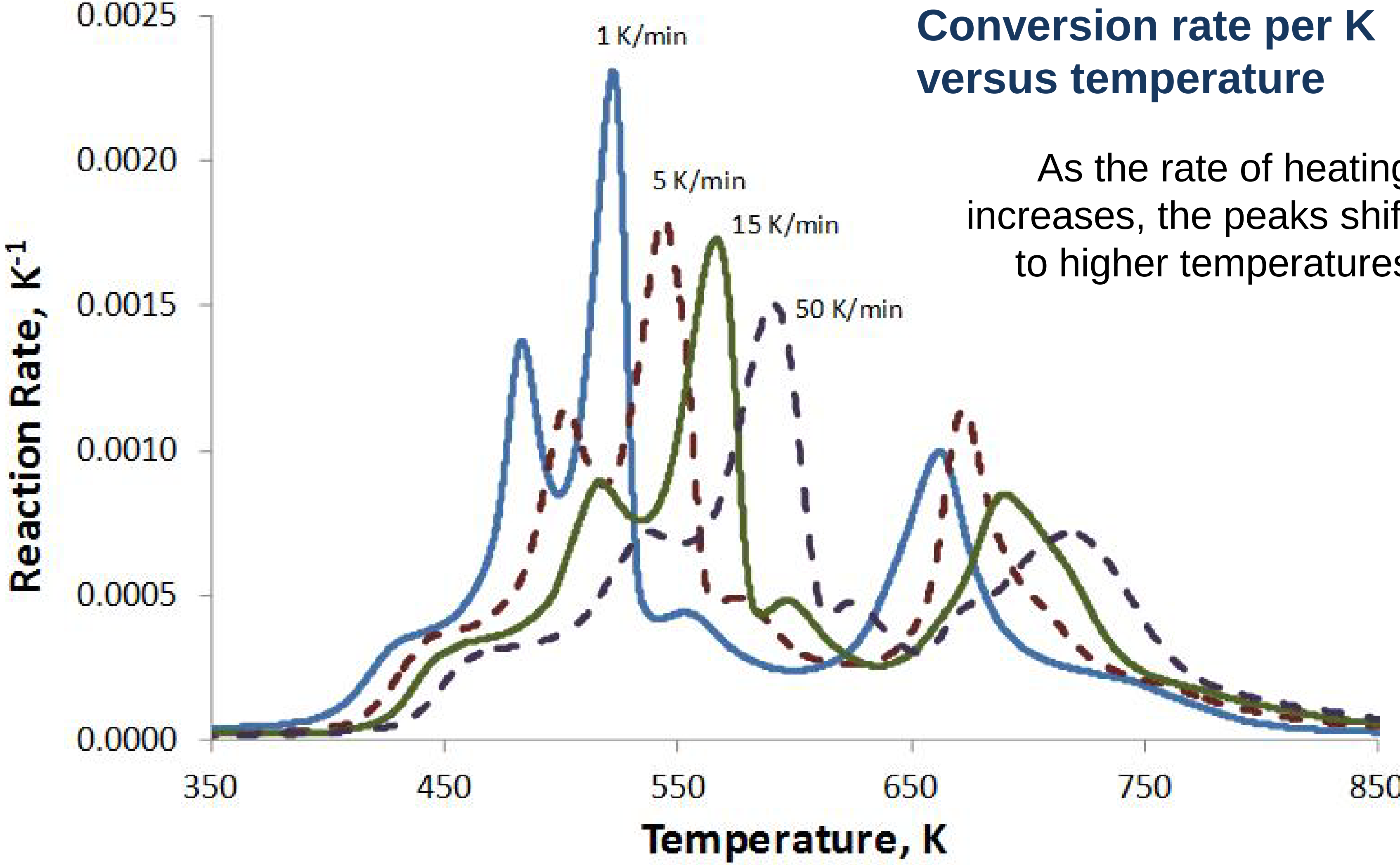
- Waste glass melter – a schematic image



TGA curves for a melter feed heated at various rates



TGA curves for a melter feed heated at various rates



Conversion rate per K versus temperature

As the rate of heating increases, the peaks shift to higher temperatures

Multiple reactions

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

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

where

the subscript *i* denotes the reaction,

x is the fraction reacted,

T is the temperature,

t is time,

B_i the i^{th} reaction activation energy,

A_i is the i^{th} reaction pre-exponential factor,

f_i is the i^{th} reaction weight,

N is the number of major reactions.

Kissinger's method

For a single first-order reaction

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

where x is the fraction reacted, Kissinger derived the following formula for the **activation energy**, B:

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

where Φ is the heating rate and T_m is the peak temperature. The pre-exponential factor, A, is given by the formula:

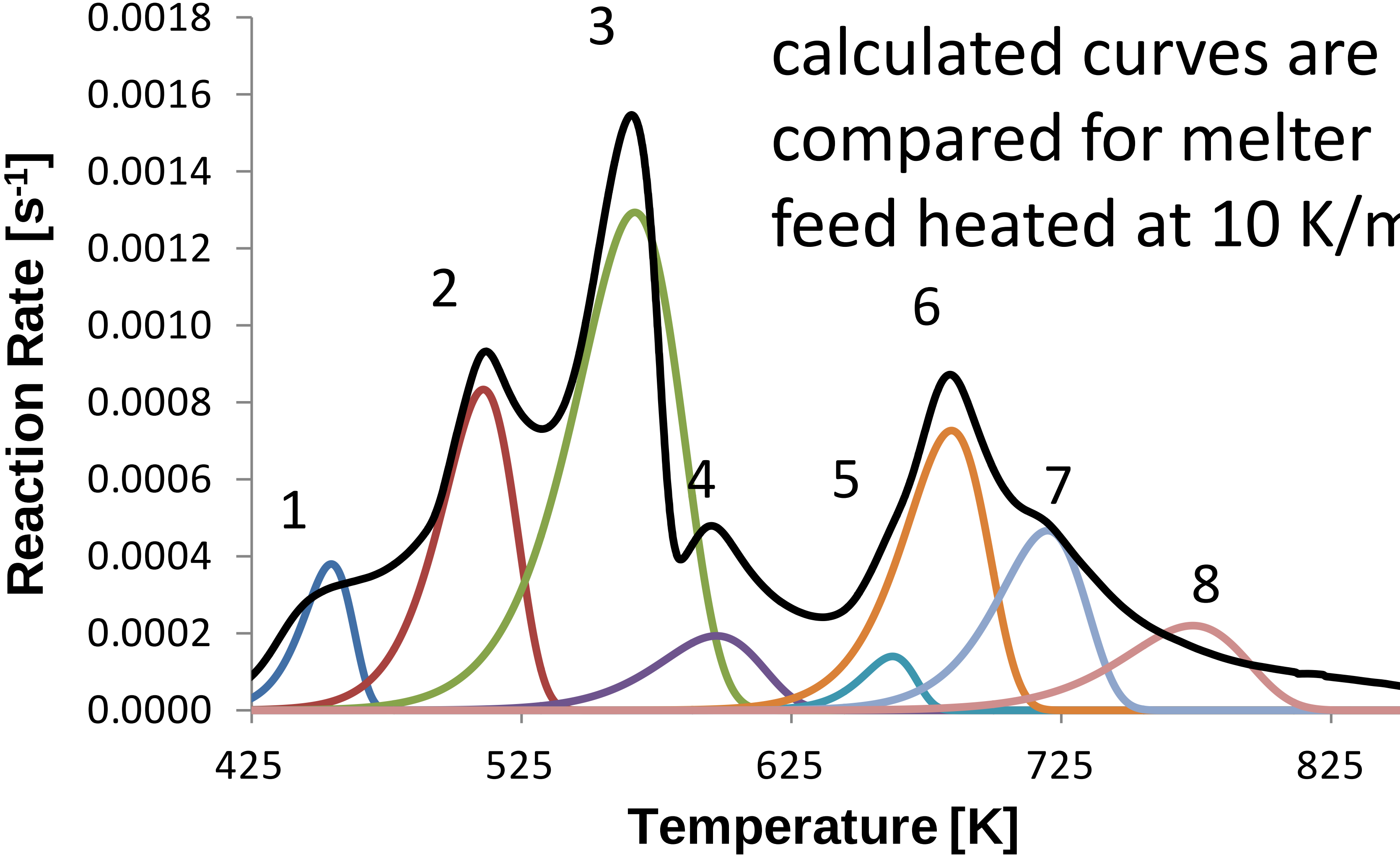
$$A = \frac{B\Phi}{T_m^2}\exp\left(\frac{B}{T_m}\right)$$

Kinetic parameters for the base 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.				

Peak deconvolution

Measured and calculated curves are compared for melter feed heated at 10 K/min



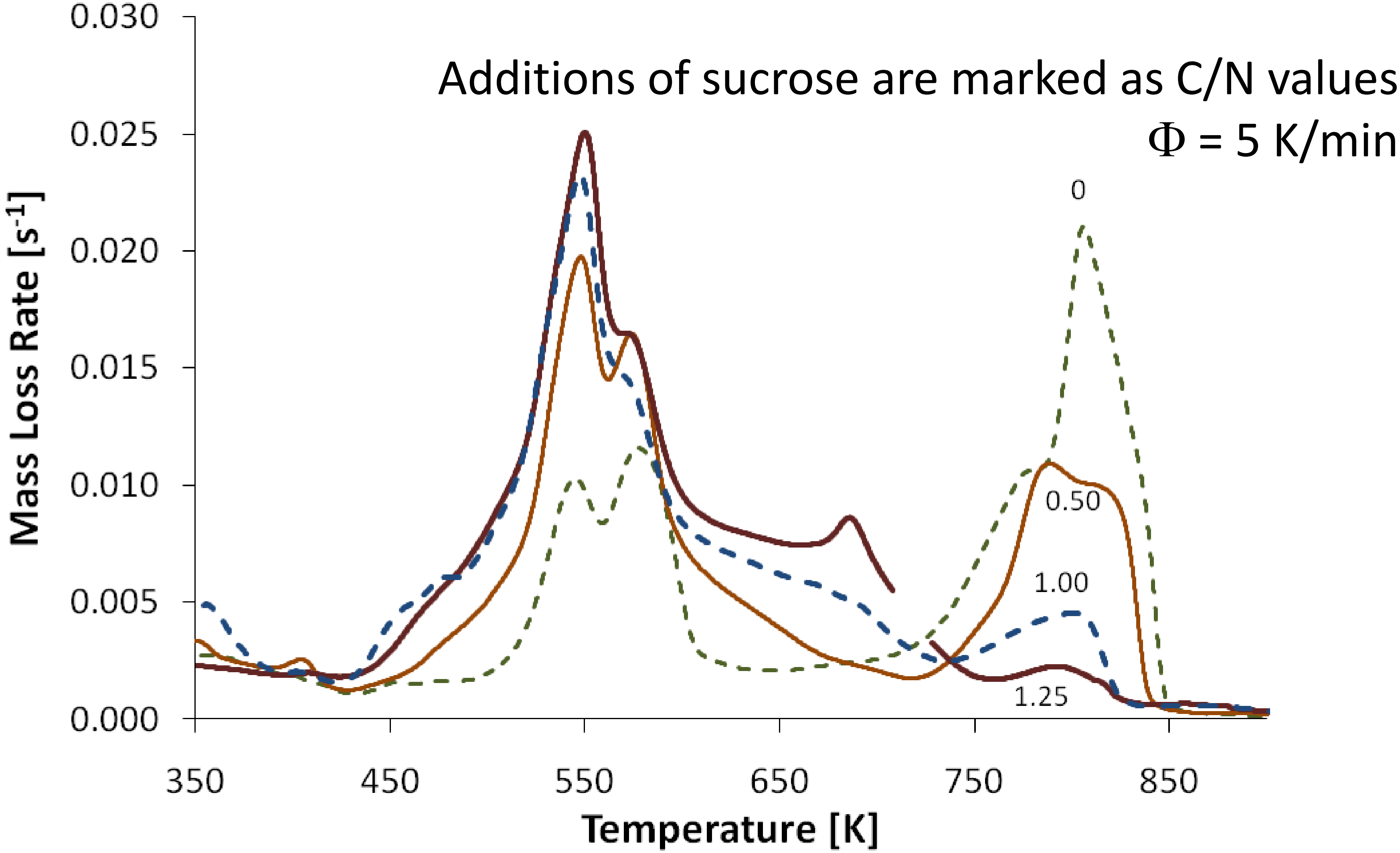
Improved model

- The next step for achieving a better fit will be to assume that the **reactions are *n*th order**, where n_i is a fitting parameter.

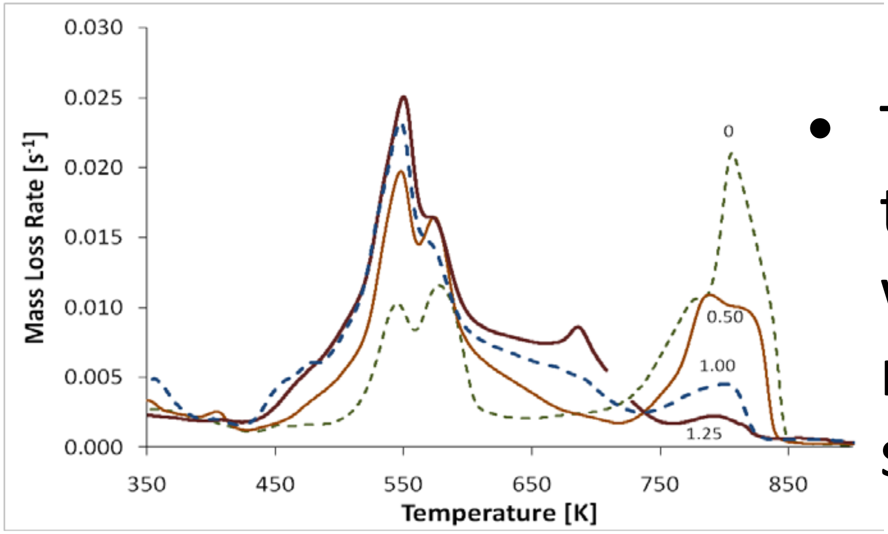
$$\frac{\mathrm{d}x}{\mathrm{d}t} = \sum_{i}^{N} f_i A_i (1 - x_i)^{n_i} \exp\left(-\frac{B_i}{T} \right)$$

- Each reaction ideally has single values of B_i, A_i, f_i, and n_i, even though subsequent reactions may be affected by preceding reactions.
- As Φ increases, slow reactions become less complete and new reactions may occur.

Sucrose addition



Effect of C/N ratio



- The irregular peaks at 450 to 575°C (725 to 850 K) were caused by the reaction of nitrates with silicates and borates.

•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.

•Somewhat higher C/N would be necessary to destroy all nitrates.

CONCLUSIONS

- The TGA allows activation energies to be obtained for major melter-feed reactions.
- Adding sucrose shifts the gas release to lower temperatures by destroying nitrates.
- 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.

Redox and foaming

- **Foaming** is caused by oxygen-evolving reactions at $T > 900°C$.
- Reducing **multivalent oxides** would decrease foaming.
- This can be achieved by adding more **reducing agents** than needed for nitrate destruction.