Ceramic Engineering 122
Glass Batching, Melting, Casting and Annealing

OBJECTIVE
The objective of this lab is to familiarize the student with the processing of simple oxide glasses using traditional melting and casting procedures.

ELEMENTS:
- Batch calculation and preparation
- Glass melting and casting
- Annealing of as-cast glasses

PRINCIPLES DEMONSTRATED
- Techniques for preparing glasses from the melt.

MATERIALS AND EQUIPMENT
- Raw materials: Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$, H$_3$BO$_3$, SiO$_2$,
- Fireclay crucibles; Sample bags

SUGGESTED READING
- James E. Shelby, Introduction to Glass Science and Technology, ARC Paperbacks, U.K. (1997); Chapter 3

Background
Attached to this handout are the class notes from the CER103 section on glassmaking. These notes provide useful background information about this lab activity, including descriptions of common batch materials and examples of batch calculations.

Experimental Procedure

1) Calculate appropriate batch compositions for the glasses to be prepared by your lab group; see below, all assigned compositions given in mole%. Determine the weights of raw materials needed to prepare 75g samples for each glass. **BRING YOUR BATCH CALCULATIONS TO CLASS ON Feb. 3rd** and include copies of your batch calculations in your lab report, due on February 10, 2004.

ALL COMPOSITIONS IN MOLE% 

Group 1: **Boyce, Gilmore, Seiter, Volek**
- 25% Li$_2$O 25% B$_2$O$_3$ 50% SiO$_2$
- 25% Na$_2$O 25% B$_2$O$_3$ 50% SiO$_2$
- 25% K$_2$O 25% B$_2$O$_3$ 50% SiO$_2$
Group 2: Amelung, Heller, McCoy, Yang
20% Na$_2$O 30% B$_2$O$_3$ 50% SiO$_2$
30% Na$_2$O 20% B$_2$O$_3$ 50% SiO$_2$
40% Na$_2$O 10% B$_2$O$_3$ 50% SiO$_2$

Group 3: Malone, Marchegiani, Muller, Rodelas
20% Na$_2$O 20% B$_2$O$_3$ 60% SiO$_2$
25% Na$_2$O 25% B$_2$O$_3$ 50% SiO$_2$
30% Na$_2$O 30% B$_2$O$_3$ 40% SiO$_2$

Group 4: Bundy, Daugherty, Grodsky, Walker
20% K$_2$O 30% B$_2$O$_3$ 50% SiO$_2$
30% K$_2$O 20% B$_2$O$_3$ 50% SiO$_2$
40% K$_2$O 10% B$_2$O$_3$ 50% SiO$_2$

Group 5: Fernandez, Skornia, Snyder
25% Na$_2$O 25% B$_2$O$_3$ 50% SiO$_2$
25% Na$_2$O 35% B$_2$O$_3$ 40% SiO$_2$
30% Na$_2$O 45% B$_2$O$_3$ 30% SiO$_2$

2) Tare the balance, then weigh out the appropriate amount of each raw material into plastic weighing boats. Keep the area around the balance clean. Add each weighed raw material to a beaker and mix thoroughly, using a spatula, to obtain a homogeneous batch.

3) **Safety Note:** Protective gloves and face shields should be worn while working with the furnaces and molten glass. Do not wear sandals. Guard against being hit by thermally shocked glasses flying off the table.

4) Pour batch into a fireclay crucible (no more than 1/2 full), and place into a glow-bar furnace that has been pre-set at 1200°C. **USE A CATCH CRUCIBLE and avoid contact with the furnace heating elements.** Allow the batch to decompose for approximately 10 minutes before removing the crucible from the furnace and adding more batch material. Repeat these steps until the entire batch has been added to the crucible. Melt for 30 minutes, or until the batch is completely decomposed and fluid. (Note that some compositions may require longer melting/fining times and maybe higher melting temperatures.) Do not overfill the crucible during melting or a portion of the batch may foam out of the crucible and be lost, which will alter the final glass composition.

**NOTE:** If you spill any glass into the furnace or if any batch material foams over and out of the catch crucible- **notify the GTA immediately.**

5) All glass should be cast onto stainless steel plates, which are available in the furnace lab. The melt should be poured into several bars and patties for future analyses.
Some bubble-free samples must be cast, for use in future labs. NOTE: IT IS VERY IMPORTANT THAT YOU POUR AT LEAST TWO BARS THAT ARE 1" LONG, ~1/4" SQUARE. THESE SAMPLES WILL BE USED FOR THERMAL EXPANSION MEASUREMENTS. Note 2: Thermal shock may be a problem, if so, it may be necessary to preheat the stainless steel plates prior to casting.

6) Make observations about your melt and the as-cast samples. For instance, is your melt fluid? Is your glass free of bubbles? Is there any evidence of phase separation and/or crystallization? These observations will be useful when preparing your lab report.

7) As-cast samples should be placed in an annealing oven immediately after casting. The annealing oven should be preheated to 525°C prior to casting. The samples should be held at 525°C for at least 30 minutes before turning the oven off. Samples can be removed from the oven after it has cooled to room temperature (~10 hours). Again, take notes about the appearance of the glasses after annealing.

8) Samples should be removed from the annealing oven (once cooled) and observed under cross-polarized light. Only samples free of interference patterns should be considered fully annealed. Samples that were not completely annealed should be re-annealed at a higher temperature (i.e., 575°C) to ensure that the glass is free of residual stresses.

9) All annealed samples should be placed in labeled, plastic bags.

10) The same procedures (steps 2 through 9) should be repeated until all three glasses have been prepared.

11) Do not discard your crucibles. They will be used in a subsequent lab.

12) CLEAN UP THE LAB! Do not leave samples and crucibles lying about. Be sure that the area around the balance is free from spilled batch materials.

13) All data will be compiled by the GTAs and posted on the web at:

   http://www.umr.edu/~brow/cer122_data.html

Report

The reports for the first four ‘glass melting’ segments will be brief (2 or 3 pages at most) reviews of the procedures and results from each segment. Each student will write an individual report, but should collaborate on the collection and interpretation of the results.

Each report will include the following:
Introduction and Purpose Statement:
- Explain the purpose of the laboratory exercise and review pertinent background information (if any) gleaned from textbooks or course notes.

Experimental Procedures
- Provide experimental details- how a sample was made (raw materials, processing conditions, etc), how an experiment was run, how a property was measured, etc.
- Discuss uncertainties associated with your measurements; include statistical information if possible.

Results and Discussion
- Make observations about the melts and samples- Did one batch take longer to fully melt than another? Was one melt more viscous than another? Was one composition more prone to devitrification? Did you notice if your crucible reacted with any of the melts? (What effect might that have on your glass?) Did one composition require a higher annealing temperature? Did everything work out just as planned?
- Whenever appropriate, use graphs and tables to present your results- and be sure to note the statistical significance of your data.
- Can you explain trends in your results based on what you know of the effects of glass composition on properties? Can you provide a citation to a textbook or course notes to support your explanation?

Summary
- Summarize the most significant results of this lab segment- If you were writing this for a boss on a job, what are the most important points you would want that boss to understand from your work.
- Provide suggestions for improving your experiments or for other experiments that might support the conclusions you have drawn or might provide interesting results.

Appendices
- Add to your report copies of important results; for example, your batch calculations.
- Include answers to the following questions as an appendix to your report:
  1. Describe the decomposition reactions that occurred when your batch materials converted to the melts. What chemical reactions are occurring as your batch converts to a melt?

Your ‘glass pieces’ will be worth 25 points and the report worth 50 points.

Each student will prepare an individual report. The report is due **Tuesday, February 10th** in class.
Glass Making

- Raw materials
- Batch calculations

**Batch**: mixture of unmelted raw materials. Batches are heated and melted to form **melts**, which are then cooled to form **glasses**.

- High purity, high quality chemicals; generally expensive per volume
  - Research melts
  - Optical glasses
  - Low volume, high tech applications
- Less pure minerals
  - Commodity commercial glasses
  - High volume/low cost
  - Glass plants are located around the country to reduce shipping costs- commodity materials are low cost/low margin materials

---

**Glass Making Raw Materials**  
(Glass Researcher 5(2) 1996)

**Quantity:**

- >20 million tons in North America in 1994.
- Sand: ~15 million tons
- Limestone: 680,000 tons
- Dolomite: 114,000 tons

**Costs:**

- $0.01-0.06/pound
  - Sand, feldspar, limestone, soda ash
- $0.15-0.60/pound
  - Potash, KNO₃, TiO₂, BaCO₃, ZnO, Pb₃O₄, zircon
- $1.50-13.00/pound
  - Cobalt/nickel oxides, sodium antimonate, cerium compounds

Examples of important raw materials for commercial glasses are shown in Table 3-1 in Shelby's book. Among the more significant ones are:

- Feldspars (albite: Na₂O; anorthite: CaO; aplitite: R₂O/RO)
- Borax (borosilicate glasses)
- Dolomite
- Limestone
- Nepheline
- Kyanite (aluminosilicate fiber glasses)
- Sand
- Soda ash

Cullet (recycled glass) is another important commercial batch ingredient

- 20-40 wt% of batch
Shelby classifies **five types of batch components:**

1. **Glass forming oxides:** usually the dominant compositional constituent
   - \( \text{SiO}_2, \text{B}_2\text{O}_3, \text{P}_2\text{O}_5 \), etc.
2. **Fluxes:** reduce melting temperatures
   - \( \text{Na}_2\text{O}, \text{PbO}, \text{K}_2\text{O}, \text{Li}_2\text{O} \), etc.
3. **Property modifiers:** added to tailor chemical durability, expansion, viscosity, etc.
   - \( \text{CaO}, \text{Al}_2\text{O}_3 \), etc.
4. **Colorants:** oxides with 3d, 4f electron structures; minor additives (<1 wt%)
5. **Fining agents:** minor additives (<1 wt%) to help promote bubble removal
   - As-, Sb-oxides, \( \text{KNO}_3, \text{NaNO}_3, \text{NaCl} \), fluorides, sulfates
   - Minor effect on bulk properties, but important processing additive for commercial (large scale) production.

### Batch Melting Processes

1. **Release of gases**
   - Gases expand to large volumes: \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \)↑
   - One mole limestone: \( \sim \text{37 cm}^3 \) \( \text{CaO} \)
     \( \sim \text{22,400 cm}^3 \) \( \text{CO}_2 \)
   - Gases produce a considerable stirring/homogenization effect
2. **Formation of liquid phases**
   - Direct melting of batch components
   - Melting of eutectic mixtures
     - **Eutectic:** (Greek: *easily melted*): lowest point on the solid-liquid diagram
     - freezing point depression (another reason to study P. Chem.)

   ![Eutectic Reactions Reduce Melting Temperatures](image)

   - Melting of Cullet
     - Note: liquid phase reactions are much faster than solid-state reactions; addition of cullet, fluxes accelerate various batch reactions
3. **Volatileization of melt components**
   - Oxide (liquid) → Oxide (gas)
   - Alkali oxides (Li<Na<K<Rb<Cs (the latter a problem for HLW melting))
• Pb, B, P, halides have relatively high vapor pressures
• Glass composition can vary from that expected from the batch-losses reduced at lower temperatures.

4. Fining Reactions: removing bubbles
• Gases trapped in interstices between particles
  • Fine sands (or batch components): lots of bubbles
• Gases created by batch decomposition reactions
• Gases created by refractory corrosion reactions, etc.
• Bubbles created by precipitation from melts with supersaturated gases

a) Removal of bubbles by buoyancy effects
• Rate of bubble rise: \( V_b \sim (g \Delta \rho r^2)/3\eta \) (Shelby eq. 3.3)
  • \( g \) is gravitational constant;
  • \( \Delta \rho \) is density difference between gas and melt;
  • \( r \) is bubble radius
  • \( \eta \) is viscosity
• bubbles rise faster in fluid melts
• large bubbles rise faster than small ones

b) Removal of bubbles using fining agents: chemical method
• Releasing large quantities of gas to sweep away small bubbles
• Remove oxygen from bubbles, reducing them below critical size where surface tension eliminates the smallest

• Arsenic, antimony oxides are efficient fining agents
  • Added as 0.1-1.0 wt\% As_2O_3, Sb_2O_3; work in series of reactions:
    • Batch rxn: \( 4\text{KNO}_3 + 2\text{As}_2\text{O}_3 \rightarrow \text{K}_2\text{O} + 2\text{As}_2\text{O}_5 + 4\text{NO}↑ + \text{O}_2↑ \) (Large bubbles generated by these reactions sweep away small ones)
    • Increasing the melt temperature reduces the oxide:
      • \( \text{As}_2\text{O}_5 \rightarrow \text{As}_2\text{O}_3 + \text{O}_2↑ \) more bubbles are swept away
    • Reducing the process temperature reverses the equilibrium:
      • \( \text{As}_2\text{O}_3 + \text{O}_2 \rightarrow \text{As}_2\text{O}_5 \) : this pulls \( \text{O}_2 \) out of remaining bubbles (reduction in internal pressure causes bubbles to collapse below critical size (0.1 mm) where surface tension eliminates the rest.)
• As, Sb are toxic, so other temperature dependent fining reactions are often used:
  • sulfates: \( 2\text{SO}_3 ↔ 2\text{SO}_2 + \text{O}_2↑ \)
  • \( 4\text{CeO}_2 ↔ 2\text{Ce}_2\text{O}_3 + \text{O}_2↑ \)
**Batch Calculations**

1. calculate glass composition in mole% or weight%
2. calculate the batch composition needed to produce a glass with a specified composition (mole% or wt%)
3. calculate the glass composition that will result from melting a specific batch.

**General Concepts:**
- account for weight loss resulting from batch decomposition reactions
  - carbonates (-CO$_2$)
  - hydrates (-H$_2$O)
  - nitrates (-NO$_x$)
  - sulfates (-SO$_x$)
- e.g., soda ash: Na$_2$CO$_3$ → Na$_2$O + CO$_2$
- dolomite: CaCO$_3$•MgCO$_3$ → CaO + MgO + CO$_2$

(Such raw materials contribute their respective oxides to a glass composition).

The weight of a glass is less than the weight of a batch
Typically 12-20 wt% loss for a commercial melt

Shelby tabulates ∆wt using his *Gravimetric Factors* ($G_i$):

\[
G_i = \frac{\text{Molar Weight(raw material)}}{\text{Molar Weight(oxide)}} \Rightarrow \text{weight (raw material)} = \text{weight (oxide)} \cdot G_i
\]

i.e., How much limestone is needed for 100 grams CaO?

\[
\text{wt CaCO}_3 = \text{wt. CaO} \cdot G_i(\text{CaCO}_3) = 100 \text{ grams} \cdot 1.78 = 178 \text{ grams CaCO}_3 \text{ for 100 grams CaO}
\]

i.e., How much CaO is provided by 100 grams CaCO$_3$?

\[
\text{wt CaCO}_3 = \text{wt. CaO} \cdot G_i(\text{CaCO}_3) = 100 \text{ g} \cdot 1.78 = \text{wt. CaO} = (100 \text{ grams})/1.78 = 56.2 \text{ grams CaO from 100 grams CaCO}_3
\]

Glass compositions are expressed as oxides- so the first step to any batch calculation is to determine which and how much oxide is contributed by a batch component.

Note: some raw materials contribute more than one oxide:
- dolomite: CaCO$_3$•MgCO$_3$ → CaO + MgO + CO$_2$
  
  1 pound dolomite → 1 pound/3.29 → 0.304 pounds CaO
  → 1 pound/4.58 → 0.218 pounds MgO

  (1 *mole* dolomite → 1 mole CaO + 1 mole MgO)
Note: some oxides might come from more than one raw material:
- SiO$_2$ will be supplied by sand, feldspar, kyanite, etc.
- Need to keep track of all sources of all oxides

Example of a batch calculation: (see Shelby pp. 32-33)

1. Calculate the composition (wt% and mole%) of a glass obtained by melting 120 grams of K$_2$CO$_3$, 80 grams of limestone (CaCO$_3$), and 400 grams of silica.

   Calculate amount of oxide obtained from each raw material:
   \[ \text{wt. K}_2\text{O} = \frac{\text{wt K}_2\text{CO}_3}{\text{mol. wt. K}_2\text{CO}_3}/\text{mol. wt. K}_2\text{O}} = \frac{\text{wt K}_2\text{CO}_3}{\text{Grav. Factor. K}_2\text{CO}_3} = \frac{120 \text{ g K}_2\text{CO}_3}{138.2 \text{ g K}_2\text{CO}_3/\text{mol}}/\frac{94.2 \text{ g K}_2\text{O}}{\text{mol}} = 81.6 \text{ g K}_2\text{O} \]
   \[ \text{wt CaO} = \frac{80 \text{ g CaCO}_3}{1.78 \text{ g CaCO}_3/\text{g CaO}} = 44.9 \text{ g CaO} \]
   \[ \text{wt. SiO}_2 = \frac{400 \text{ g SiO}_2}{1.00 \text{ g SiO}_2/\text{g SiO}_2} = 400.0 \text{ g SiO}_2 \]

2. Convert to wt%:

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$O</td>
<td>15.5</td>
</tr>
<tr>
<td>CaO</td>
<td>8.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>76.0</td>
</tr>
</tbody>
</table>

3. Convert to mole%:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$O</td>
<td>10.4</td>
</tr>
<tr>
<td>CaO</td>
<td>9.6</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>80.0</td>
</tr>
</tbody>
</table>

Note: reverse the calculation to determine the batch composition needed for a particular glass composition.