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Glass Science Tutorial
Lecture #6: The Melting of Silicate Glasses, a Review of Selected Topics

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and Waste Management

Westinghouse Hanford Company
Richland, Washington

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

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Dr. E. Lowell Swarts,
Lecturer

Date Published
March 1995

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The Melting of Silicate Glasses, a Review of Selected Topics

(Outline)

Lecture to be Presented at Westinghouse Hanford Company, March 21-22, 1995

Dr. E. L. Swarts

1. Introduction
   1.1 Historical perspective
   1.2 Traditional glass-making = art + science/engineering
   1.3 LLW glass-making, in need of decoupling/independent control of processes
   1.4 The LLW Process - special needs/characteristics
   1.5 DISCLAIMER: Not a comprehensive review, partially redundant

2. The Melting
   2.1 Compositions
   2.2 Batch materials criteria
   2.3 Hatch materials sources
   2.4 Special considerations re the LLW process
   2.5 Primary reactions
   2.6 Melting of batch on molten glass (Siemens Tank)
   2.7 All-electric melters: "cold-top" design
   2.8 Melting accelerators

3. Foam (With P. Hrma at Battelle Northwest, Coals to Newcastle?)
   3.1 A problem in Siemens melting
   3.2 Origins
   3.3 Mechanisms of formation/decay
4. **Refining (Bubble Removal)**

4.1. Interaction of gases with commercial silicate melts
4.2. Solubility and diffusion of gases in glass
4.3. Removal of bubbles from molten glass

5. **Homogenization (Reduction of Chemical Heterogeneity to Acceptable Levels)**

5.1. Terminology
5.2. Degree and kind of heterogeneity in different products
5.3. Methods of detection
5.4. Sources of heterogeneity
5.5. Homogenization Mechanisms
Melting of Silicate Glasses: a Review of Selected Topics

Lectures Presented at Westinghouse Hanford Company,
March 21-22, 1995

E. L. Swarts

1. Introduction
   1.1 A very brief historical perspective: from obsidian to LLW

   1.2 Glass-making = art + science/engineering, the proportions changing over the years, depending on product.
      1.21. SiO₂ the ideal glass for many applications, but too hard to fabricate into needed shapes economically.
      1.22. Addition of alkali lowers viscosity.

   Fig. 1. The soda-silica binary

   1.23. Other additions yield specific properties, e.g., color (transition elements), low expansion coefficient (B), optical properties (Pb, rare earths), durability (Al).

   Fig. 2. The S-L-S ternary

   1.24. Early technology ⇒ crude mixtures melted in small clay pots, holding and stirring ⇒ required homogeneity, with high technical aids of potatoes and green wood!
1.25. Especially in last 100 years, art replaced (partially) by science

⇒ today's low cost commodities, e.g., float glass, light bulbs, insulation and reinforcement fibers, blown or pressed containers, tableware, e.g., Corning's Corel "sandwich" structure), borosilicate laboratory and industrial chemical containers.

⇒ high tech optical fibers, low expansion telescope mirrors, packages for electronic devices, etc.

⇒ encapsulants for nuclear waste (Saclay-France, Savannah River, West Valley, Hanford).

1.3. Still more science needed, melting/refining / forming, due to coupling/overlap of different processes ⇒ lack of independent control, e.g., melting reactions, refining, homogenization, thermal conditioning for forming

Fig. 3. Overlap of processing in traditional glass-making

1.4. LLW encapsulation process not likely not as demanding of some steps, e.g., small bubble removal, but far more demanding, e.g., with respect to emissions, refractory interactions

1.5. Disclaimer: This review will suffer from incompleteness on subjects relevant to LLW needs and
deals mostly with Na$_2$O-CaO-SiO$_2$ (S-L-S) compositions made in large float furnaces by sulfate fining technology.

2. The Melting Process

2.1. Some typical commercial compositions: 50-75% SiO$_2$ + alkali, alkaline earths, alumina, boric oxide, minor components $\Rightarrow$ specific properties

Fig. 4. Typical commercial compositions

2.2. Batch materials criteria

- availability/costs (including beneficiation, transportation)
- impurity level tolerance
- particle size requirements of the melting process (avoiding segregation in the batch that exacerbates inhomogeneity, yielding carry-over from dusting, causing refractory runnagge, plugging checkers of a Siemens tank, controlling reaction times)
- volatilization/pollution, e.g., F (fiberglass), SO$_x$, NO$_x$, Se ("bronzel" float glass)

2.3. Batch material sources

- silica $\Leftarrow$ natural sands: "dirty" sand less expensive than "clean" sand (compare West Coast sand with Ottawa, Penna, Kona)
alkali ⇔ soda ash (\(\text{Na}_2\text{CO}_3\)), currently mostly from natural trona deposits in Wyoming; also caustic soda (50% aqueous \(\text{NaOH}\))

- alkaline earths ⇔ limestone (\(\text{CaCO}_3\)), dolomite (\(\text{CaCO}_3 \cdot \text{MgCO}_3\))
- alumina ⇔ feldspars, nepheline syenite, kaolin, blast furnace slag (\(\text{CaO} - \text{MgO} - \text{SiO}_2 - \text{Al}_2\text{O}_3\)), calcined/hydrated \(\text{Al}_2\text{O}_3\)
- boric oxide ⇔ borax (\(\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3\)), natural borate minerals, boric acid
- cullet ⇔ process waste, recycling, application related to purity requirements
- melting accelerants / fining agents / redox control ⇔ salt cake (\(\text{Na}_2\text{SO}_4\)), \(\text{Sb}_2\text{O}_5 +\) nitrates, blast furnace slag
- colorants ⇔ transition metal oxides, impurities or deliberate additions (for final product properties or process control)
  - LLW components ⇒ nitrates, nitrites?; cations?

2.4. Special considerations re the LLW process

- components of LLW ⇔ redox control of melting
  - " " " " radiation transfer during melting
- durability versus cost ⇒ lower alkali, higher \(\text{Al}_2\text{O}_3, \text{B}_2\text{O}_3\)?
- particle sizes $\leftarrow$ specific LLW process:
conventional process considerations $\Rightarrow$ reaction rates, cost,
furnace carry-over problems

Fig. 5. Effect of grain size on melting time

2.5. Primary reactions (dependent upon composition
and process: for "vanilla" S-L-S in a Siemens tank

2.51. Carbonate reactions (studied in great detail,
many reports of laboratory results and proposals for
fundamental reaction paths: not likely significant to LLW
process development

- formation of eutectics possible in
principle, but particle size differences and inter-particle
wetting may interfere

- CO$_2$ evolution, thermally and from
reaction with sand grains stirs the melting mixture

2.52. Final sand dissolution, the limiting step

- limited by diffusion kinetics of SiO$_2$ into
the viscous final composition
- SiO$_2$ diffusion gradient sensitive to batch
additives (melting accelerators)
2.6. Melting of Batch on Molten Glass (Siemens Tank)

*Fig. 6. Schematic elevation view of a generic Siemens tank*

*Fig. 7. Approximate temperature profile, Siemens tank*

2.61. Batch logs heated from above: primary energy $\rightarrow$ direct radiation from the flames and re-radiation from the crown (Hammel/Takahashi)

*Fig. 8. Ablation melting (Hammel)*

outermost layer at highest temperature $\Rightarrow$ thin foam
- below the foam, with decreasing $T$, a liquid layer containing undissolved batch, a few mm thick
- within 2-3 cm, unreacted batch at near room temp (!)

2.62. Run-off or ablation of outer liquid phase

- highly dependent upon batch shape,
  melting limited by the rate at which the liquid layer runs off, exposing cold, unreacted batch

*Fig. 9. Effect of shape on ablation rate (Hammel)*

- obviously dependent upon furnace $T$:
  $1300^\circ C \Rightarrow 1550^\circ C$ doubles rate
Fig. 10. Effect of $T$ on ablation rate

2.63. Heating of batch from below by hot glass

Fig. 11. (same as Fig. 6)

- dependent upon radiant heating characteristics (emissivity) of the glass, e.g., on its $\text{FeO}_x$ content
- dependent upon movement of hot molten glass

2.64. The "Spring Zone" $\Rightarrow$ tank flows

- temperature coefficient of density for a generic S-L-S melt
  \[ \sim 2.38 \text{ g/cm at } 1100^\circ\text{C} \]
  \[ \sim 2.33 \quad " \quad 1450^\circ\text{C} \]

- small $\Delta$ in density $\Rightarrow$ a large volume of slowly flowing molten glass from hotter to colder regions

Fig. 12. Density-driven longitudinal flows

- energy input, distribution $\Rightarrow$ "hot-spot"

- molten glass cools at cold walls / bottom and under surface of batch $\Rightarrow$ setting up a complex slow-flow circulation system within the tank
Fig. 13. Three dimensional flows

2.65. Radiation heat transfer from above $\propto \Delta T$ between flames/crown and glass surface and limited, but enhanced by

- bubbling from below lifts cold glass

Fig. 14. Bubbling to enhance heat transfer

- electric boosting

Fig. 15. Electrical boosting

2.7. All-electric melters, e.g., "cold-top" designs

Fig. 16. Generic submerged throat electric melter

Fig. 17. Cold-top melter (Woolley)

2.71. Advantages include

- much better control of volatilization
- higher energy efficiency
- control of internal flows within the tank

2.72. Disadvantages include
- higher cost of electrical energy
- generally faster refractory erosion

2.8. Melting accelerators

2.81. Liquid additions to batch ⇒ intimate mixing/faster reaction

- H₂O (usually ≤ 4 wt%) prevents dusting and segregation, helps distribute water-soluble species, e.g., alkali, around sand grains ⇒ faster melting, but at additional cost of energy required to dry the batch

Fig. 18. Energy cost of H₂O addition to batch

- partial replacement of alkali by caustic soda (50% aqueous NaOH) ⇒ advantages / disadvantages of batch wetting (less carbonate to be decomposed, but cost premium over soda ash)

- fossil fuel oil ⇒ no batch dissolution, but added energy to the melting process

2.82. Minor additions to the batch, e.g., Li₂O, B₂O₃, F ⇒ fluidity of the melt, but usually with

- cost premium for the batch
- increased refractory corrosion
- environmental problems
2.83. Additions of SO₃ as "salt cake" (Na₂SO₄) or gypsum (CaSO₄·2H₂O), at a level ~0.2% final glass wt.claimed by some to react with carbonates

⇒ lower melting eutectic (liquid) phase ⇒ faster
dissolution of sand grains

- claimed by others to inhibit initial sand
grain dissolution due to coating of those grains, retarding
their reaction with carbonates

- net dissolution effect likely dependent
upon amount of addition and grain size of the sand

- act like a wetting agent

Fig. 19. Acceleration of melting by salt cake

- generate Liesegang ring-like SO₃-rich
shells around dissolving sand grains ⇒ acceleration of
dissolution more complex than by simple wetting
(Hammel / Bloss at PPG)

Fig. 20. S-rich rings around dissolving sand
grains (Hammel/Bloss)

- facilitate removal of bubbles from
dissolving sand grains, preventing their flotation and
formation of a "silica scum"

Fig. 21. Bubble removal from sand grains in lab
melts
- plus chemical reducing agents, e.g., powdered coal or graphite, or blast furnace slag containing sulfides $\Rightarrow$ decompose $\text{Na}_2\text{SO}_4$ at lower temperatures $\Rightarrow$ faster melting (but irrelevant as one lowers salt cake additions to meet emissions limits)

2.84. Cullet (scrap glass) addition

- advantageous, requires $\sim$60% of the total energy required for raw batch

*Fig. 22. Cullet melting advantage*

- disadvantage: melting cullet $\Rightarrow$ viscous phase in the batch pile $\Rightarrow$ ablation

- disadvantage: cullet in the batch pile $\Rightarrow$ reduces its insulating characteristics $\Rightarrow$ decreases $\Delta T$ between heat source and batch surface $\Rightarrow$ slower ablation

- disadvantage: cullet particles compete with undissolved sand grains for reaction with alkali $\Rightarrow$ slower sand dissolution

- disadvantage: presence of too high proportions of cullet $\Rightarrow$ difficulty in bubble removal: mechanisms complex, but related to $\text{SO}_3$ refining

- in practice, the % cullet $\Leftarrow$ compromise between necessary recycling and efficient furnace operation
- has yielded widely varying claims of melting acceleration in pilot-scale trials
- requires additional capital investment and operating costs for the pelletizing equipment.
- not widely used in commercial practice.

3. Foam

3.1 A problem in Siemens melting

- insulation of the molten glass from the radiation from flames and crown, reduction of up to 60% in energy transfer
- limitation of maximum crown temperature ⇒ slower melting/less complete refining

3.2 Origin
- bubble raft from melting covers melt

Fig. 23. Foam in a Siemens tank

- bubble generation from batch reactions

3.3 Mechanisms of formation

3.31. Decomposition of carbonates? Very small scale lab experiments with carbonates and remelted cullet (Kappel et al.) ⇒
2.85. Pre-compaction of batch by pelletizing, forming into briquettes or pellets

- requires additives, e.g., caustic soda to "glue" the batch together and yield pellets strong enough to withstand handling
  - reduces dusting and carry-over
  - may increase efficiency by allowing preheating from exhaust gases
  - drastically changes the insulating properties of the batch as it enters the furnace
  - subject to many plant trials
- stable CO2 bubble foams that decay exponentially in time.

Fig. 24 Decay of foam (Kappel et al.)

- decay of foam dependent upon thinning of bubble laminae (viscosity)

Fig. 25. Thinning of bubble laminae (Kappel et al.)

- but Kappel's foam decay constant apparently ∝ glass composition in a complex manner

Fig. 26. Foam decay constant vs viscosity (Kappel et al.)

- presence of SO₂ ⇒ accelerated foam decay

3.32. Decomposition of sulfates

- in float tanks, foam ⇔ sulfate content of batch, decomposition: higher sulfate in batch ⇒ more foam

- foam generation linked by Hrma et al. to sulfate level, sand grain size, rates of temperature increase of the melt, and SO₃ levels in the glass.

- two foam generation mechanisms related by Hrma et al. to different forms of sulfate in the melt
Fig. 27. Foam volume vs time, fine sand (Kim and Hrma)

Fig. 28. Foam volume vs time, coarse sand (Kim and Hrma)

- conclusion by Hrma et al.: foam $\Leftarrow$ sand grains and bubble growth
- in float tanks, stable formation near the hot spot at least from the bubble nucleation mechanism
- very small additions of alumina $\Rightarrow$ decreased solubility of $\text{SO}_3$, more foam at lower temperatures
- irrespective of details, sulfate-containing melts $\Rightarrow$ stable foams $\Rightarrow$ interfere with the process
- foams destabilized by flames, reducing agents, e.g., carbon or water spray

3.33. Alkali-iron-alumino-borosilicate simulated NWG compositions studied at Battelle Northwest (Goldman)

- reboil pressure $\propto$ higher dissolved $\text{H}_2\text{O}$ and $\text{O}_2$
- in the foam major, $\text{O}_2$, lesser $\text{N}_2$, and $\text{H}_2\text{O}$
- differences in glass viscosity not responsible alone for differences in foam stability.
- foams destabilized by reducing agents
- experience with foaming at Battelle
3.4. Melting process for LLW ← collective experience at Northwest, Savannah River, Saclay (France), different compositions, melting processes

4. Refining (Bubble Removal) [An overlapping process with final sand grain dissolution: bubble defects likely not critical in, LLW process, but gaseous interactions likely important]

*Fig. 29. (Fig. 3 again)*

4.1. Interaction of gases with commercial silicate melts

4.11. Why important?
   - ratio of volume of evolved gases to volume of glass ≤ 200: gases released upon melting TV glass (Krämer) ⇒ major CO₂ (carbonates), O₂, NO₂ (nitrates), at higher T, O₂ (Sb₂O₅) ⇒ Sb₂O₃

*Fig. 30. Release of gas from a TV glass batch*

   - major combustion products from gas/oil firing, CO₂, H₂O, (N₂)
   - fundamental properties and melting technology remarkably dependent on interactions with several species

4.12. Dissolution of H₂O
   - of all gases, most completely characterized
Fig. 31. Important reviews, \( H_2O \) in glass

- in conventional silicate glasses melted under ambient pressure, total dissolved \( H_2O \) \( \leq \sim 0.1\% \)
- strong near IR OH absorption in three bands

Fig. 32. Near IR spectra, \( H_2O \) in vitreous \( SiO_2 \) and S-L-S glass (Scholze)

Fig. 33. Near IR spectra, \( Al_2O_3 \) additions to S-L-S glass (Scholze)

- total absorption \( \propto (P_{H2O})^{1/2} \) at equilibrium
- dissolution mechanism in acidic (high \( SiO_2 \)) melts \( \Rightarrow \) depolymerization of \( SiO_2 \) network, analogous to effect of alkali \( \Rightarrow \) decreased viscosity

\[ \equiv \text{Si-O-Si} \equiv + HOH \Rightarrow 2 \equiv \text{SiOH} \]  \hspace{1cm} (1)

Fig. 34. Effect of \( H_2O \) on viscosity of a S-L-S glass (Scholze)

- increased solubility in more basic melts accounted for by conversion of non-bridging oxygens

\[ \equiv \text{Si-O}^- + HOH \Rightarrow \equiv \text{Si-OH} + OH^- \]  \hspace{1cm} (2)
\[ O^-^2 + HOH \Rightarrow 2OH^- \]  \hspace{1cm} (3)

Fig. 35. \( OH^- \) sites in S-L-S glass (Scholze)
- many other effects, e.g., rate of crystallization, phase separation (Shelby et al.)
  - slightly increasing solubility with \( \uparrow \) T
  - in float glass, \( \sim 0.035\% \text{ H}_2\text{O} \).
  - geological compositions equilibrated under high temperature and pressure \( \Rightarrow \) total \( \text{H}_2\text{O} \) contents of 1 - 10\%, near IR absorption from molecular \( \text{H}_2\text{O} \) and combination bands.

**Fig. 36. Higher levels of \( \text{H}_2\text{O} \) in** \( \text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2 \) glasses (Stolper et al.)

**Fig. 37. Higher levels of \( \text{H}_2\text{O} \), molecular and hydroxyl, in \( \text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2 \) glasses (Stolper et al.)

4.13. Dissolution of \( \text{CO}_2 \)
- \( \text{Na}_2\text{O}-\text{SiO}_2 \) melts, landmark results by Pearce \( \Rightarrow \) solubility increases with \( \uparrow \) alkali,

**Fig. 38. Solubility of \( \text{CO}_2 \) in \( \text{Na}_2\text{O}-\text{SiO}_2 \) melts** (Pearce)

\[
\begin{align*}
\text{CO}_2 + \equiv\text{Si-O}^- \quad &\Rightarrow \equiv\text{Si-CO}_3^- \\
2\equiv\text{Si-CO}_3^- \quad &\Rightarrow \equiv\text{Si-O-Si}= + \text{CO}_3^{2-} \\
\end{align*}
\]

- solubility decreases with \( \uparrow \) temperature (decreasing stability of the \( \text{CO}_3^{2-} \) group)
- in melts of conventional lower-alkali silicates, dissolved \( \text{CO}_2 \) orders of magnitude less than measured by Pearce (10-100 ppm ??)
- in geological magmas, molecular CO₂ also seen

*Fig. 39. IR absorptance of CO₂ in Na₂O-Al₂O₃-SiO₂ glasses (Stolper et al.)*

*Fig. 40. Pyrolysis of CaO-MgO-SiO₂ glasses containing CO₂ (Rai et al.)*

- addition of H₂O ⇒ higher CO₂ solubility as CO₃⁻², perhaps by depolymerization of highly acidic structure

\[
\text{≡Si-O-Si} + \text{HOH} \Rightarrow 2 \equiv\text{SiOH} \quad (1)
\]

\[
\equiv\text{SiOH} + \text{CO₂} \Leftrightarrow \equiv\text{Si-CO₃}^- + \text{OH}^- \quad (???) \quad (6)
\]

- addition of Al₂O₃ ⇒ decreased dissolved CO₃⁻², likely due to polymerization of structure

\[
2 \equiv\text{Si-CO₃}^- + \text{Al₂O₃} \quad \text{(with alkali)} \Rightarrow 2 \equiv\text{Al-O-Si} + 2 \text{CO₂} \quad (7)
\]

4.13. Dissolution of N₂

- ambient and neutral to oxidizing conditions ⇒ very low physical solubility: estimated at 0.1 ppm (Mulfinger)

- reducing conditions ⇒ chemical dissolution, characteristic near IR absorption at sufficiently high concentration
Fig. 41. N in S-L-S glass, 2 hr at 1400OC (Mulfinger)

Fig. 42. IR absorptance of N in S-L-S glass (Mulfinger)

- proposed chemical dissolution mechanisms

\[ \equiv \text{Si-OH} + \text{NH}_3 \Rightarrow \equiv \text{Si-NH}_2 + \text{H}_2\text{O} \]  
\[ + \equiv \text{Si-OH} \]  
\[ \downarrow \]  
\[ (\equiv \text{Si-})_2 \text{NH} + \text{H}_2\text{O} \]  
\[ + \equiv \text{Si-OH} \]  
\[ \downarrow \]  
\[ (\equiv \text{Si-})_3 \text{N} + \text{H}_2\text{O} \]  

- chemical dissolution of N\textsubscript{2} ⇒ removal of H\textsubscript{2}O

Fig. 43. Removal of H\textsubscript{2}O from glass by chemical dissolution of N\textsubscript{2} (Mulfinger)

- N\textsubscript{2} chemical solubility ↑ with increasing T and increasing acidity

Fig. 44. N\textsubscript{2} solubility vs T and \text{SiO}_2 content in Na\textsubscript{2}O-Si\textsubscript{2}O\textsubscript{2} glasses (Swarts)
- in metallurgical slags with strong reduction, N-3 is present in two modes.

Fig. 45. N\textsubscript{2} dissolved as N-3 in CaO-MgO-SiO\textsubscript{2} slags (Martinez and Sano)
- oxynitride glasses an important technological development

4.14. Dissolution of S (SO\textsubscript{3}, SO\textsubscript{2}, S\textsuperscript{-2})
- dissolved species and concentration dependent on redox and composition

Fig. 46. S in Na\textsubscript{2}O-SiO\textsubscript{2} glasses (Nagashima and Katsura)
- under oxidizing conditions,

\[
\text{SO}_2 + \frac{1}{2}\text{O}_2 \Rightarrow \text{SO}_3
\]
\[
+ \equiv\text{Si-O}^- \Rightarrow \equiv\text{Si-SO}_4^-
\]

Fig. 47. Raman spectra of SO\textsubscript{4}\textsuperscript{-2} in glass (Konijnendijk and Buster)
- at high T, SO\textsubscript{3} dissociates \Rightarrow lower solubility

\[
\text{SO}_3 \Rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2
\]
- under reducing conditions,
\[ H_2S + \equiv Si-O^- \Rightarrow \equiv Si-S^- + H_2O \quad (14) \]

\[ \equiv Si-S^- + Fe^{+3} \Rightarrow \text{beer-bottle amber at} \]
\[ P_{O_2} < \sim 10^{-7} \text{ atm} \]

- dissolved \( SO_4^{-2} \) removed by dissolution of \( H_2O \) at high \( T \) (Hanke and Scholze)

\[ \equiv Si-SO_4^{-2} + 3 \equiv Si-O-Si\equiv + 2H_2O \Rightarrow \]
\[ 4 \equiv Si-OH + 2 Si-O^- + SO_2 + 1/2 O_2 \quad (15) \]

**4.15. Dissolution of \( O_2 \)**

- most important dissolution mechanism
chemical, through equilibria of variable valence species in the melt, e.g., S, Sb, and transition metals.

\[ 2 FeO + 1/2 O_2 \Leftrightarrow Fe_2O_3 \quad (16) \]
\[ Sb_2O_3 + O_2 \Leftrightarrow Sb_2O_5 \quad (17) \]
\[ Ce_2O_3 + 1/2 O_2 \Leftrightarrow 2 CeO_2 \quad (18) \]
\[ 2MnO + 1/2 O_2 \Leftrightarrow Mn_2O_3 \quad (19) \]

- color and radiation transfer sensitive to transition metal equilibria, e.g., Fe and Cr

*Fig. 48. \( Fe^{+2} \) and \( Fe^{+3} \) spectra in glass*
*Fig. 49. Extinction coefficients for \( Fe^{+2} \) and \( Fe^{+3} \) in glass*

- detectable physical solubility
Fig. 50. Extraction of physical and chemical $O_2$ from glass (Stelzner et al.)

4.16. Dissolution of reducing species, e.g., $H_2$

$$\text{Fe}_2\text{O}_3 + H_2 \Rightarrow 2\text{FeO} + H_2O \quad (20)$$

$$\text{Sb}_2\text{O}_5 + \text{CO} \Rightarrow \text{Sb}_2\text{O}_3 + \text{CO}_2 \quad (21)$$

$$=\text{Si}-\text{O}-\text{Si}= + H_2 \Rightarrow 2=\text{Si}-\text{OH} - \quad (22)$$

4.17. Dissolution of He, Ne, Ar
- physical solubility, small but detectable
- diffusivity highly dependent upon size
- useful as structural probes, comparing molecular pore size distribution in glass structures, e.g. by Shelby, Shackelford, et al.

4.2 Characterization of solubility and diffusion of gases in glass

4.21. Problems in characterizing dissolved gases
- failure to attain equilibrium
- inadequate control of redox conditions
- problems with analytical procedures and very low levels of most gases dissolved in glass

4.22. Solubility measurements
- solubility constants, S-L-S compositions
Fig. 51. Solubility constants of gases in S-L-S glasses (Krämer)

Fig. 52. Concentrations of gases dissolved in commercial compositions (Krämer)

- temperature coefficients of solubility

Fig. 53. Temperature coefficients of solubility

4.23. Diffusion measurements

- diffusion constants, S-L-S compositions

Fig. 54. Diffusion constants of gases in S-L-S glasses (Krämer)

Fig. 55. Shrinkage of He bubbles in molten glass (Frischat)

- equilibration of electrolytic O₂ bubbles in molten glass ⇒ very sensitive detector of dissolved gases

Fig. 56. Detection of physically dissolved N₂ and Ar dissolved in float glass equilibrated with air (Swarts)

4.24. Analytical methods and limits

- H₂O: IR spectroscopy (requires knowledge of absolute extinction coefficients) ⇒ ~ 0.01%, nuclear magnetic resonance an "absolute " method
24

- SO₃ : X-ray fluorescence (requires use of standards analyzed by wet chemistry) $\rightarrow \sim 0.005\%$.
- CO₂, N₂, O₂ : physical hot extraction procedures $\rightarrow ?$ (large uncertainty)

4.3. Removal of bubbles from molten glass

4.31. Bubbles usually the most important defect in commercial products.

- small concentrations (wt\%) of a gaseous species $\Rightarrow$ a large volume of bubbles.
- primary melting $\Rightarrow$ a foamy mass, hundreds of small bubbles/in³
- in final commercial products, bubble levels 5-8 orders of magnitude fewer; TV faceplates and automotive windshields most critical (in windshield glass from a top-performing float tank, rejectable bubbles, > 0.2-0.5mm, < 1/ ft³
- what level will be required in LLW product?

4.32. Early history of bubbles

- air originally in the batch displaced by decomposition products, H₂O, CO₂, SO₂, N₂, O₂ before any refining chemistry becomes active
- in a large float tank, bubbles from melting carried forward from under the batch toward upward flowing "spring-zone" generated by the hot spot
Fig. 57. Flows toward the spring-zone
Fig. 58. Typical bubble concentrations uptank of the spring-zone of a large float tank

- bubble contents $\Rightarrow$ major CO$_2$, minor N$_2$, from primary melting

Fig. 59. Gas analyses, bubbles from dip samples

- in a cold-top melter?

4.33. Primary fining mechanism - flotation

$$v \propto r^2 \frac{\rho}{\mu}$$  \hspace{1cm} (23)

where $v$ = velocity of rise
$r$ = radius of the bubble
$\rho$ = glass density
$\mu$ = glass viscosity

- viscosity limited by temperature and composition
- bubble size increased by fining chemistry

4.34. Sulfate fining mechanism.

- warming of glass in spring zone
- decomposition of dissolved sulfate
SO $\Rightarrow$ SO$_2$ + O$_2$ \quad (24)

- enlargement of bubbles $\Rightarrow$ faster rise

Fig. 60. Enlargement of bubbles by sulfate fining

4.35. Oxygen fining mechanism

- warming of glass in spring zone
- reduction of dissolved oxygen source

Sb$_2$O$_5$ $\Rightarrow$ Sb$_2$O$_3$ + $[1/2 \text{O}_2]$ \quad (25)

+ [Fe$_2$O$_3$ $\Leftarrow$ FeO]

- enlargement of bubbles $\Rightarrow$ faster rise
- significantly different from sulfate mechanism, requires more oxidizing conditions than usually used with sulfate

4.36. Effectiveness of flotation mechanisms dependent upon the flow systems

- in a Simens tank, glass flows to the hot spot through the spring-zone
- in a cold-top melter, internal flows are determined by electrode location and power distribution
4.37. A Secondary Fining Mechanism, bubble shrinkage, significant with $O_2$ fining

- for bubbles not removed by flotation, cooling of the glass in the conditioner $\Rightarrow O_2$ reaction with dissolved lower valence species.

$$O_2 \text{ (bubble)} + Sb_2O_2 \text{ (glass)} \Rightarrow Sb_2O_5 \text{ (glass)} \quad (26)$$
$$\Rightarrow \text{bubble shrinkage}$$

- problem, diffusion of other gases from solution in the glass into bubbles.

*Fig. 61. Interdiffusion of gases between bubble and melt*

4.38. Bubble shrinkage also previously proposed as a secondary refining mechanism in sulfate refining.

- in principle, $SO_2$ remaining in bubbles should resorb into the glass at lower temperatures

$$"SO_2 + \frac{1}{2}O_2" \text{ (bubble)} \Rightarrow SO_3 \text{ (glass)} \quad (27)$$

- picture is more complex in float glass (mildly reduced): $O_2$, $SO_3$, and $SO_2$ not generally found in bubbles

- deposits of $Na_2SO_4$ and elemental $S^0$ frequently present
- bubbles in float tanks survive over long
life-times in the tank

Fig. 62. Deposits in bubbles (float glass)
Fig. 63. Na$_2$SO$_4$ and elementary S°
Fig. 64. Calculated partial pressures of
elemental S° present in bubbles from float glass dip
samples

- subtle sulfur chemistry at work, likely not
applicable to any practical LLW process, but included here
as illustrative of subtle chemistry found through glass-
making

In principle  
\[3\text{SO}_2 \Leftrightarrow 2\text{SO}_3 + \frac{1}{2}\text{S}_2\]  \hspace{1cm} (28)

At a typical conditioner temperature, 1100°C,
\[\Delta F^\circ = +321 \text{ kJ and } \therefore \text{ not spontaneous}\]

With alkali present

\[3\text{SO}_2 + 2\text{Na}_2\text{O (glass)} \Leftrightarrow 2\text{Na}_2\text{O}_4 + \frac{1}{2}\text{S}_2\]  \hspace{1cm} (29)

for which \(\Delta F^\circ = -398 \text{ kJ at 1100 °C and } \therefore \text{ spontaneous,}\nthus accounting for rapid loss of SO$_2$ from bubbles by a
mechanism other than absorption, and little importance of
bubble shrinkage
3. In contrast to a conventional S-L-S float glass, in a low-alkali E-fiberglass composition, SO$_2$ the major bubble gas and without deposits or shrinkage

4.39. CO$_2$/N$_2$ exchange between bubbles and surrounding glass an important phenomenon in melting of commercial products: its significance again likely much less important in any LLW process, but the subtlety of the chemistry is again illustrative

- in TV glass, a major CO$_2$ bubble $\Rightarrow$ mostly N$_2$ in relatively short time.

Fig. 65. Exchange of gases between bubble and melt, O$_2$-fined TV glass (Krämer)

- N$_2$ exchange between molten glass and primary CO$_2$ bubbles in a container tank dependent upon T correlated with the dissolved N content of the glass, consistent with the known dependence of N solubility upon T

Fig. 66. Dissolved N$_2$ vs location in glass from a container tank (Debras et al.)

Fig. 67. Correlation of dissolved N$_2$ with N$_2$ in bubbles taken from same locations (Debras et al.)
4.40. Shrinkage of very small bubbles $\Leftarrow$ surface energy, probably not important for LLW processing but again illustrative of subtle processes

- the pressure inside a bubble is increased by surface tension (analogous to the slight increase inside a soap bubble or balloon) according to the relation

$$p_{st} = \frac{2\sigma}{r}$$

(30)

where $p_{st} =$ the pressure increase,
$\sigma =$ the glass surface tension
$r =$ the bubble radius

- for S-L-S glass this effect of significance only for bubble diameters less than $\sim 0.1$ mm (!), but likely responsible for dissolution of smallest seed in some commercial products.

Fig. 68. Pressure increase within a bubble due to surface tension

5. **Homogenization**

5.1. Following final sand dissolution and bubble removal to acceptable levels, variation in chemical composition $\Rightarrow$ troublesome heterogeneity, affecting color, density, and refractive index
5.12. Terminology

- "striae" = two-dimensional layers of composition different from the surrounding matrix
- "cords" = one-dimensional veins that differ in composition
- "scale" = describes dimensions.
- "intensity" refers to difference in composition.

Fig. 69. Schematic representation of scale and intensity (Cooper)

5.13. Degree and kind of heterogeneity that is acceptable \(\iff\) product

- in containers, uneven coefficients of expansion \(\Rightarrow\) internal stresses \(\Rightarrow\) degraded strength \(\Rightarrow\) million $ litigation settlements
- in automotive windshields and architectural glass, varying refractive index \(\Rightarrow\) unacceptable distortion
- in optical glass, index differences \(\Rightarrow\) degraded instrument performance
- in the LLW product, effects listed above not important, but homogeneity required to maintain structural integrity without cracking (increased surface area) of the finished shapes, irrespective of how they are encased

- schlieren photography

Fig. 70. Striagrams of plate glass

- chemical etching/interferometry

Fig. 71. Use of chemical etching and interferometry

5.15. Sources of heterogeneity

- batch upsets, e.g., errors
- inappropriate grain size of raw materials
- inadequate mixing
- segregation in the batch.
- volatilization at the atmosphere surface, e.g., preferential loss of alkali or B$_2$O$_3$
- change in redox conditions at the atmosphere surface, e.g., amber streaks on the top surface of float glass
- reaction with refractories, dissolution of SiO$_2$, Al$_2$O$_3$, and ZrO$_2$

5.16. Homogenization Mechanisms

- diffusion down the concentration gradients

Fig. 72. Schematic representation of reduction of concentration differences by diffusion
- mixing (deformation of striae and cords by shear and stretching) $\Rightarrow$ shorter diffusion paths $\Rightarrow$ faster leveling of concentration gradients

Fig. 73. Reduction of heterogeneity by attenuation and diffusion

- mixing and diffusion by shear and stretching obtained through complex flow patterns in the tank, mechanical mixing and long residence times

6. Oxidation/Reduction Reactions

6.1. Common Observations

6.1.1. Properties of melts and resulting glasses $\Leftarrow$ oxidizing or reducing conditions during melting, e.g., with nitrates or with coal in the batch.

- heat transfer within the melt
- foaming characteristics
- refining properties
- color of a resulting glass $\Leftarrow$ relative concentrations of different valence state ions from the same element, e.g., $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$

6.1.2. Valence state ratios may depend upon

- the atmosphere in contact with the melt
- base composition of the glass
- processing time

6.13. Different valence states readily detectable in melts and glasses

- spectrophotometry
- wet chemical/instrumental methods

6.2. Characterization of oxidation/reduction processes

6.21. Redox reactions of a multivalent species, e.g., Fe, with O₂ may be represented

- most simply, by

\[
\begin{align*}
\text{Fe}^{+2} & \iff \text{Fe}^{+3} + \text{e}^- \\
4\text{Fe}^{+3}(\text{melt}) + 2\text{O}^{-2}(\text{melt}) & \iff 4\text{Fe}^{+2}(\text{melt}) + \text{O}_2 (\text{gas})
\end{align*}
\]

(31) (32)

where \(\text{O}_2(\text{gas})\) refers to molecular O dissolved in the melt or available to it from an equilibrating atmosphere, and \(\text{O}^{-2}\) represents O chemically bonded in the glass structure

- still more accurately, by acknowledging that generally these ionic species coordinate with O of the melt structure ⇒ equilibrium equations written in terms of those coordinated groups.

6.22. Rigorously, the redox relationship in a silicate melt is described in terms of the effective
concentrations or activities of the different species
(denoted by brackets) and an equilibrium constant \( K \), e.g.,
for Fe,

\[
K_{Fe} = \frac{[Fe^{+2}]^4 [O_2]}{[Fe^{+3}]^4 [O^-]^2}
\]

(33)

where one
- approximates activities of Fe by using
analytically measured concentrations
- sets the melt's oxide ion activity, \([O^-] = 1\)
for melts sufficiently dilute that the redox ion addition does
not significantly change the oxidic glass structure

6.3. Effect of impressed \( P_{O_2} \)

6.3.1. For the equation as written, a lower partial
pressure of \( O_2 \) \( \Rightarrow \) more reduction, a larger value of
\([Fe^{+2}]\), and a smaller \([Fe^{+3}]\)

\[
\text{Fig. 74. } Fe^{+3}/Fe^{+2} \text{ vs } P_{O_2} \text{ (Johnston)}
\]

6.3.2. Generalizing for element \( M \) that may yield
the lower and higher oxidation states \( M^{(m-n)+} \) and \( M^{m+} \)
and following Schreiber's convention

- the equilibrium may be expressed

\[
4M^{m+}_{(\text{melt})} + 2nO^- \leftrightarrow 4M^{(m-n)+}_{(\text{melt})} + nO_2(\text{gas})
\]

(34)
- the equilibrium constant becomes

\[
K_M = (M^{m-n+}_{\text{melt}})^4 (P_{O2})^n / (M^{m+}_{\text{melt}})^4 (O^2)^{2n}
\]

(35)

with measured concentrations and the O\(_2\) partial pressure denoted by parentheses

6.33. Dependencies of many multivalent couples upon redox conditions have been determined.

_Fig. 75. Redox ratios of multivalent ions vs P\(_{O2}\) (Shreiber)_

- significance: from the equilibrium expression from above (Equation 34), one may derive the relation

\[
\log[M^{(m-n)+}_{\text{melt}} / M^{m+}_{\text{melt}}] = \\
n/4(-\log P_{O2}) + B(\text{constant})
\]

(36)

- thus, a plot of

\[
\log [M^{(m-n)+}_{\text{melt}} / M^{m+}_{\text{melt}}] \text{ vs } (-\log P_{O2})
\]

yields a slope of 4/n and predicts n, the number of e- transferred in the redox reaction. As will be seen below, interpreting the this equation in terms of its net free energy of reaction and the thermodynamic cell potentials permits the use of the constant B to quantitatively compare the ease
of reduction of different elements in a silicate melt.

6.4. Temperature dependence: holding the impressed $P_{O_2}$ constant with no significant change in $(O^{2-})$ of the glass, higher temperatures $\Rightarrow$ stronger reduction of the multivalent element

6.41. From fundamental thermodynamics (Clausius-Clapeyron and van't Hoff equations) one can derive the relation

$$\log K = -\Delta H^0/RT + C \quad (37)$$

where $K$ = the equilibrium constant for the reaction
$\Delta H^0$ = change in heat content for the reaction as written
$R$ = the gas constant
$T$ = temperature
$C$ = an integration constant

This formulation may be applied to redox equilibria by substituting for $K$ the ratio of concentrations of the redox species $(M^{m+}_{\text{melt}}) / (M^{(m-n)+}_{\text{melt}})$ and wrapping the $(P_{O_2})$ and $(O^{2-})$ terms into the integration constant.

6.42. Results from Johnston's experiments

Fig. 76. Temperature dependence of equilibrium constants (Johnston)
6.43. Characterization of redox levels in commercial glasses

Fig. 77. Equilibration of commercial float glasses in air (Swarts)

Fig. 78. Temperature dependence of redox ratio in commercial float glass

- these data together with the Johnston results \Rightarrow estimate of the redox level in commercial float glass, an effective \( P_{O_2} \) in the range 10^{-3} to 10^{-4} atm

6.5. Compositional dependence, an apparent paradox

6.51. Experiments \Rightarrow making alkali-silicate melts at 1400°C more acidic, e.g., more SiO_{2}-rich, increases Fe^{2+}

Fig. 79. Redox ratio vs basicity (Baucke and Duffy)

Similar behavior reported for other redox species in dilute solution

6.52. In apparent contradiction with experimental results, inspection of the redox equation for Fe from above

\[
4Fe^{3+}_{(melt)} + 2O^{2-}_{(melt)} \Leftrightarrow 4Fe^{2+}_{(melt)} + O_2(gas)
\] (32)
leads one naively to expect that increasing the SiO₂ content should decrease a melt's ionicity (O²⁻), thus increasing Fe³⁺.

- in fact, the redox equation as written does not describe real life in the melt: Fe²⁺ and Fe³⁺ do not exist as bare ion species in the melt, but are coordinated to the O²⁻: The extent of that coordination depends upon the composition.

- various authors have proposed formal treatments by which to rationalize this difficulty, and indeed, Schreiber has also reported data for Fe at much lower temperatures that are apparently at odds with previous results.

6.6. Interactions between redox couples

6.61. One simple interaction between the Sn and Fe couples in float glass  ⇒  patent for blue glass

Fig. 80. Redox ratios for Sn and Fe (Johnston)

High-temperature melting led to a higher concentration ratio of Sn²⁺/Sn⁴⁺ than for Fe²⁺/Fe³⁺. However, upon cooling the glass to lower temperature without otherwise changing the internal PO₂ a lower Sn²⁺/Sn⁴⁺ is favored relative to the Fe²⁺/Fe³⁺, and Fe³⁺ is reduced to Fe²⁺, yielding its characteristic red absorption and a blue glass. This kind of interaction has been described analytically by Rüssel and Schreiber.
6.62. Practical NWG compositions must contain a witches brew of redox couples, the interactions of which must be complex and which will determine affect melting behavior, e.g., foaming and radiant heat transfer. The Fe2+/Fe2+ couple has been proposed (Goldman and Iwase) to serve as an overall indicator of the internal redox state, assuming that it comes to equilibrium with other couples.

6.7. Characterization of redox behavior by reduction potentials.

6.71. From fundamental free energy considerations, the half reactions describing a redox process in the glass melt can be characterized by the reduction potential $E^\circ$

$$4M^{m+}_{(melt)} + 4ne^- \rightarrow 4M^{(m-n)^+}_{(melt)} \quad E^\circ_{M} \quad (38)$$

$$nO_2 \text{ (gas)} + 4ne^- \rightarrow 2nO^{2-}_{(melt)} \quad E^\circ_{O} \quad (39)$$

Combining Equations 37 and 38 yields

$$4M^{m+}_{(melt)} + 2nO^{2-}_{(melt)} \rightarrow 4M^{(m-n)^+}_{(melt)} + nO_2 \text{ (gas)} \quad (40)$$

with a $\Delta E^\circ_{MO} = E^\circ_{M} - E^\circ_{O} \quad (41)$

One may compare the behavior of different cation redox couples under the same conditions of sufficiently dilute solution and temperature by setting the $E^\circ_{O}$ for each
reaction at the same common reference value, by convention = 0. Following Schreiber's convention, one then derives $E'_M$ (a simple function of the reduction potential $E'_M$) for each couple, defined by the relation

$$\log \left[ \frac{M^{m-n}+(\text{melt})}{M^m(\text{melt})} \right] = \frac{n}{4}(-\log P_{O2}) + E'_M \quad (42)$$

where $E'_M$ is equivalent to the constant $B$ of Equation 36 above.

6.72. In practice, one determines the left hand redox ratio by wet chemistry or instrumental procedures after equilibrating the melt under different $P_{O2}$, e.g., as characterized by different CO$_2$ / CO atmospheres. The linear plot of the measured log(redox ratio) versus log $P_{O2}$ then yields $E'_M$ from the intercept at log $P_{O2} = 0$ (unit activity of O$_2$). These values then provide a comparison of the ease of reduction of different species in the same melt under same conditions of temperature and effective $P_{O2}$ and predict interactions between those couples.

6.73. The determined $E'_M$ values may be ordered into an electrochemical number series for a given silicate melt analogous to the well-known series for water.

Fig. 81. An electromotive series for ions in glass (Schreiber)

Fig. 82. Comparison of the electromotive series for glass and H$_2$O (Schreiber)
6.8. Direct measurement of reduction potentials, an alternate approach to comparing redox behavior

6.81. From fundamental thermodynamics, the equilibrium constant $K$ for a reversible redox reaction can be expressed by the relation

$$\log K = -\frac{nFE_0}{RT}$$  \hspace{1cm} (43)

where $n =$ the number of electrons transferred
$F =$ the Faraday constant
$E_0 =$ the standard electrode potential
$R =$ the gas constant
$T =$ temperature

By impressing a voltage that varies by a predetermined pattern, e.g., square wave voltammetry, across a cell in the melt and measuring current flow, characteristic peaks can be detected corresponding to specific electrode reactions

- for 0.5% Fe$_2$O$_3$ in a S-L-S melt at 1100°C
Rüssel found a peak potential of -560 mv corresponding to the half reaction

$$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$$  \hspace{1cm} (44)

Fig. 83. Theoretical and experimental voltammograms (Rüssel)
- for 1% Sb$_2$O$_3$ at 900°C, two peaks were found at -180 mV and -390 mV, corresponding to the two step reduction

\[ \text{Sb}^{5+} + 2\text{e}^- \leftrightarrow \text{Sb}^{3+} + 3\text{e}^- \leftrightarrow \text{Sb}^0 \]  \hspace{1cm} (45)

**Fig. 84. Voltammogram for the two-step reduction of Sb$^{5+}$**

6.82. Characterization of the O$_2^-$/O$_2$ equilibrium in a melt by in-glass Pt and Pt/O$_2$/ZrO$_2$ sensors (Schaeffer et al.)
- a direct measure of the internal redox condition
- commercially available and in use in European furnaces
- being tested by members of the Alfred Univ. CGR
- subject to practical operating difficulties, e.g., contamination by S, dissolution of the ZrO$_2$ element in the glass melt

7. Refractory/Glass Interaction (Brief Comments on Selective Topics)

7.1. Choice of Refractories

7.11. In general, a NWG melting facility needs to minimize the rebuilding of tanks and may accept the trade-off of increased capital cost of premium refractories in exchange for longer life.
- bonded (solid-state sintered) AZS blocks still used for bottom paving in commercial Siemens tanks, but in lower temperature regions where dissolution products will not directly enter the final product: probably not a candidate for a NWG melter.

- more expensive fused-cast high-Al2O3or AZS block are the conventional high-end choice for commercial furnaces melting S-L-S compositions: different formulations within these families provide cost-effective materials. Large Siemens float tanks (≥ 500 tons/day) today operate up to ten years before a rebuild.

- in principle, more dissolution-resistant materials are available. e.g., SnO2, high-Cr2O3, and high ZrO2 blocks. However, cost, thermal-shock resistance, and environmental dangers become disadvantages. What kind of compromise would be acceptable will depend on final design of the process.

7.12. Special corrosion-resistant compositions must be used in critical locations of a melting system.

- refractory blocks through which heating electrodes enter a tank (to resist effects of the higher temperature glass)
  - high wear regions, e.g., a submerged throat

7.2. Loss of refractories, generally an unavoidable problem.
7.21. Principal Modes of Corrosion, downward flow of hot glass at a side-wall ⇒ under-cutting at the triple point

*Fig. 85. Schematic of under-cutting at a side-wall and of upward drilling*

and "upward-drilling" underneath a refractory body due to presence of gas bubbles and surface energy effects

*Fig. 86. Schematic of upward drilling*

- in conventional Siemens tanks, the glass layer in the bottom, especially in the hottest region of the melter becomes enriched in refractory components such as ZrO$_2$ and Al$_2$O$_3$.

*Fig. 87. Schematic of viscous refractory-reaction glass in the bottom of a Siemens melter*

This changed composition is more viscous and thus doesn't enter into the flow circulation patterns as completely as the primary glass. As long as a stable operation is maintained, without significant temperature fluctuations, this bottom layer, modified by the refractory dissolution products usually doesn't generate any problems. Conversely, a change in tank flow patterns that stirs up this glass can generate troublesome heterogeneity into the final product.
- in tanks that deliver glass through a bottom throat, corrosion glass may accumulate at the lowest level and even be drained off continuously, to maintain adequate homogeneity in the product.

*Fig. 88. Schematic of refractory-reaction glass in a submerged throat tank*

- permeation of hot glass from the tank into joints or cracks between refractory blocks may attack back-up refractories not intended for glass-contact, generating defects and inhomogeneous glass: interaction of clay sub-pavers with SO₃-containing glass

\[
\text{Al}_2\text{O}_3 / \text{SiO}_2 (\text{clay}) + \text{SO}_3(\text{glass}) \Rightarrow \text{more acidic glass} \\
\Rightarrow \text{lower solubility of SO}_3 \Rightarrow \text{SO}_2 \text{ bubbles} \quad (46)
\]

- premium back-up refractories may be justifiable in structures for LLW melting, depending upon design

7.22. Exudation from fused-cast materials, one glass/refractory dissolution mechanism

- a minor vitreous phase is present in most fused-cast refractories, deliberately engineered into the structure by the choice of minor additives, e.g., B₂O₃ in some formulations

- the presence of the minor vitreous phase represents a compromise between such factors as thermal
shock susceptibility (which translates into yield of uncracked blocks in the manufacturing process and thus cost), and resistance to glass corrosion (the more vitreous phase present generally, the faster the block corrodes

- alkali and alkaline earths from the contained glass diffuse into the interstitial glassy phase of the refractory block, making that phase more fluid

- the more fluid interstitial glass then drains faster from block into the flowing glass, destabilizes the remaining crystalline structure of the block near the glass interface, and accelerates its removal into the glass and dissolution

- bubble formation may occur within the block's vitreous phase, those bubbles' growth accelerating the expulsion of the block's glassy phase

7.3. Electrolytic refractory/glass interactions (perhaps no bearing on reactions in a LLW process, but it typifies subtle reactions that permeate glass-making and which may be a source of problems)

7.3.1. Anomalous small N₂ bubbles with some evidence of a refractory origin

- experiments in which samples of the ZrO₂·SiO₂ refractory were equilibrated against float glass documented generation of bubbles from the refractory:
Fig. 89. Sketch of lab equilibration of bonded AZS/glass and generation of bubbles

- in lab experiments, O₂ and N₂ bubbles \( \rightleftharpoons \) initial electrochemical origin of the primary bubbles and subsequent diffusive exchange of O₂ for N₂ dissolved in the glass
- plate glass exit lip (same kind of refractory) \( \rightarrow \) ribbon completely polluted by O₂ bubbles
- more recently, installation of this same kind of zircon-containing material in shallow conditioner by a major float manufacturer \( \rightarrow \) bubble-polluted ribbon
- same kind of phenomena observed by others on related materials (Bossard and Begley, Bedros et al.) and a general mechanism proposed for an electrochemical cell: current carried by Na⁺ diffusing from glass into the refractory and by e⁻ within the block.: patent issued covering a treatment to eliminate the most severe problem on starting up a new tank with unseasoned refractories

7.32. More recently, an extensive theoretical analysis with confirming experimental data presented by Baucke and Roth: critical requirement of the mechanism a presence of trace reducible ions (impurities) that can take part in the cell reaction

7.33. Evidence of a small electrolytic reaction in ZrO₂-free dense "high-purity" Al₂O₂ lab crucibles: with
Na₂O·SiO₂ melts ⇒ very small O₂ bubble generation near the crucible side walls, and evidence found for electrolytic reaction (a lab curiosity at most)

8. The Challenge in Modernizing Glass-making or Developing a New Process

8.1 Traditional glass-making ⇒ still much art, empiricism.
   - overlap of processes still a fact of life in most commercial processes
   - most traditional glass-making lags the chemically engineered industries, e.g., adequate independent control of individual processes (melting reactions, refining, homogenization, and thermal conditioning)
   - new "high-tech" glass making processes, e.g. optical fibers and electronic packaging developed with more discipline of chemical engineering / less baggage of old technology

8.2. Considerations re the LLW process

8.21. Need for characterization of waste make-up
   - nuclide composition, half-life spectrum: presumably well-characterized
   - chemical uniformity?
   - cation composition/redox characteristics?
- anion composition (nitrates, halides)?
- suspension medium (aqueous acidic, pH)?

8.22. Requirements of composition and product

- acceptance of as high a level of LLW as possible consistent with constraints of the required final composition, process operation and glass properties

- acceptable variability in composition, consistent with stable process operation and acceptable variability in ambient properties of the final glass

- ease of melting (minimum time/temperature integral)

- viscosity/temperature function appropriate to forming (canister filling?) with adequate resistance to phase separation and devitrification

- adequate resistance to aqueous leaching
- sufficiently low sensitivity of expansion coefficient to composition and temperature to minimize fracture (generation of increased surface area) and potential exposure to leaching
8.23. Constraints upon the process

- appropriate time/temperature melting integral to yield solid dissolution, homogenization, and refining adequate for long-term storage
- self-contained with respect to gaseous emissions, dust, and waste?
- acceptance of the LLW as a separate stream or premixed with glass batch?
- pre-compaction (pelletizing) of the batch?
- pre-heating?
- use of foreign or internal cullet?

8.24. Likely characteristics of the process

- not a traditional flame-fired open "bath-tub"
- relative separation of primary melting and conditioning functions, with ability to replace entire hardware components
- a concept similar to present cold-top melter with auxiliary homogenization/conditioning unit
- a "further out" electric melting concept such as stirred melting?

8.25. Advanced melting schemes

Fig. 90. The proposed Glasstech Mixmelter (Richards, figure from Barton)
- electric "scull" melting analogous to fused-cast refractory manufacture, but with a water-cooled shell (melting glass within glass)?

Fig. 91. "Scull-melter" concept

- hybrid semi-closed gas/electric system related to the Battelle Pyroflux melter?

Fig. 92. Battelle Pyroflux melter (figure from Barton)

- hybrid O-I RAMAR system?

Fig. 93. O-I RAMAR (figure from Barton)

8.26 Batch component aids to accelerate melting, consistent with redox character of the process, e.g., presence of significant nitrate components

8.27 Electrode and glass-contact materials consistent with redox character of the melt, required longevity of equipment, and ease of replacement
System $\text{SiO}_2 - 2\text{Na}_2\text{O} \cdot \text{SiO}_2$

Fig. 1. The soda-silica binary
Fig. 2. The S-L-S ternary
Fig. 3. Overlap of processing in traditional glass-making.
Table 1. Some Typical Glass Compositions

<table>
<thead>
<tr>
<th></th>
<th>Window</th>
<th>Glass-Ceramic</th>
<th>Ion Exchange</th>
<th>Borosilicate</th>
<th>Aluminosilicate</th>
<th>E-Fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>73.2</td>
<td>70.1</td>
<td>61.2</td>
<td>79.8</td>
<td>61.4</td>
<td>53.8</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>13.2</td>
<td>0.4</td>
<td>12.2</td>
<td></td>
<td>1.6</td>
<td>0.4</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>--</td>
<td>0.6</td>
<td>4.4</td>
<td>4.2</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>--</td>
<td>2.6</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CaO</td>
<td>8.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>18.2</td>
<td>15.7</td>
</tr>
<tr>
<td>MgO</td>
<td>3.5</td>
<td>2.6</td>
<td>3.6</td>
<td>--</td>
<td>--</td>
<td>4.9</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.3</td>
<td>17.9</td>
<td>17.5</td>
<td>2.1</td>
<td>17.3</td>
<td>14.5</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>--</td>
<td>4.4</td>
<td>0.7</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.0</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>13.6</td>
<td>--</td>
<td>10.3</td>
</tr>
</tbody>
</table>

(several minor constituents are not listed)

Fig. 4. Typical commercial compositions
Effect of grain size on melting time

Fig. 5. Effect of grain size on melting time
Fig. 6. Schematic elevation view of a generic Siemens tank
Fig. 7. Approximate temperature profile, Siemens tank
EFFECT OF BATCH SHAPE ON ABLATION RATES

<table>
<thead>
<tr>
<th>SHAPE</th>
<th>SURFACE TO VOLUME RATIO</th>
<th>MELTING TIME (MINUTES)</th>
<th>% RATE INCREASE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLAB (RESTRICTED FLOW)</td>
<td>0.25</td>
<td>49.5</td>
<td>---</td>
</tr>
<tr>
<td>SLAB (UNRESTRICTED FLOW)</td>
<td>0.62</td>
<td>37.3</td>
<td>24</td>
</tr>
<tr>
<td>CONE</td>
<td>0.56</td>
<td>36.3</td>
<td>27</td>
</tr>
<tr>
<td>HEMISPHERE</td>
<td>0.50</td>
<td>35.8</td>
<td>28</td>
</tr>
<tr>
<td>LOGS</td>
<td>0.73</td>
<td>34.5</td>
<td>30</td>
</tr>
<tr>
<td>TOROID</td>
<td>0.59</td>
<td>27.3</td>
<td>45</td>
</tr>
</tbody>
</table>

Fig. 9. Effect of shape on ablation rate (Hammer)
Fig. 10. Effect of T on ablation rate (Hammel)
Three-dimensional free convection flow in continuous glass melters. (a) Short wide furnace. (b) Long furnace. Source:

Fig. 13. Three dimensional flows
Fig. 16. Generic submerged throat electric melter
Vertical section view of a circular all-electric tank furnace.

Fig. 17. Cold-top melter (Woolley)
Fig. 18. Energy cost of $H_2O$ addition to batch
Effect of sulfate compounds on melting rate of standard soda-lime-silica batch

**Fig. 19. Acceleration of melting by salt cake**
ELECTRON MICROPROBE ANALYSIS OF SULFUR PROFILE AROUND A DISSOLVING SAND GRAIN

CONCEPTUAL VIEW OF PRECIPITATED Na₂SO₄ AROUND A DISSOLVING SAND GRAIN

Fig. 20. S-rich rings around dissolving sand grains
(Hammel/Bloss)
Effect of Salt Cake on Melting in Small Laboratory Pots

**No Salt Cake**
- Slowly dissolving silica scum above
- Clear glass below

**With Salt Cake**
- Widely dispersed sand grains

Fig. 21. Bubble removal from sand grains in lab melts
Fig. 22. Cullet melting advantage
Foam height $h$ (logarithmic scale) as a function of time $t$; temperature: 1100°C. static laboratory atmosphere.

Fig. 24: Decay of foam (Kappel et al.)
Decrease of the thickness of lamellae $d$ of a soda lime glass melt (no. 1) as a function of drainage time at various temperatures; $d_0$ is the initial thickness, $d_{\infty}$ is the quasi-stationary thickness of the lamellae.

Fig. 25. Thinning of bubble laminae (Kappel et al.)
 Foam decay constant $k$, as a function of reciprocal viscosity for various kinds of glasses in a static laboratory atmosphere: each point represents the mean of at least five series.

Fig. 26. Foam decay constant vs viscosity (Kappel et al.)
Variation of gas-phase volume per unit melt volume with time for isothermally heated melts with fine silica sand containing 4% of total Na₂O from Na₂SO₄. Experimental data points are fitted by Eq. (7).

Fig. 27. Foam volume vs time, fine sand (Kim and Hrma)
Variation of gas-phase volume per unit melt volume with time for isothermally heated melts with coarse silica sand containing 4% of total Na$_2$O from Na$_2$SO$_4$. Experimental data points are fitted by Eq. (8).

Fig. 28. Foam volume vs time, coarse sand (Kim and Hrma)
Release of Gases from Melting a TV Glass Batch Containing 0.5% Sb₂O₃
(after Kraemer, 1980)

Fig. 30. Release of gas from a TV glass batch
PREVIOUS REVIEWS, WATER IN GLASS


*Fig. 31. Important reviews, H₂O in glass*
Infrared Spectra of Vitreous Silica and 
Soda-Lime-Silica Glass (after Scholze, 1968)

Fig. 32. Near IR spectra, H₂O in vitreous SiO₂ 
and S-L-S glass (Scholze)
Effects of Al₂O₃ addition to a Na₂O-SiO₂ composition

1. No Al₂O₃
2-5. Progressively higher Al₂O₃ contents

Fig. 33. Near IR spectra, Al₂O₃ additions to S-L-S glass (Scholze)
Fig. 34. Effect of H₂O on viscosity of a S-L-S glass (Schoize)
FIG. 111 — Three different types of fixing of OH groups in glass (1 Å = 10^-10 m) [41.7 and 8]. The bottom part shows the dependence of IR spectra on the amount of water in the alkali—lime—silica glass SiO₂ 74 . CaO 10 . Na₂O 16 (wt.%). Curve A — initial glass, B — glass cleared with dry nitrogen, C — glass cleaned with H₂ (after Scholze [41.7]).

Fig. 35. OH⁻ sites in S-L-S glass (Scholze)
Near-Infrared Spectra of Soda-Alumina-Silica Glasses (after Silver and Stolper, 1989)

Fig. 36. Higher levels of H$_2$O in Na$_2$O-Al$_2$O$_3$-SiO$_2$ glasses (Stolper et al.).
Water, Dissolved as Molecules and OH Groups in Na$_2$O-Al$_2$O$_3$-SiO$_2$ Melts (after Silver and Stolper, 1989)

Fig. 37. Higher levels of H$_2$O, molecular and hydroxyl, in Na$_2$O-Al$_2$O$_3$-SiO$_2$ glasses
Solubility of CO₂ in Soda-Silica Melts
(after Pearce, 1964)
Infrared Absorbance of Na$_2$O-Al$_2$O$_3$-SiO$_2$ Glasses, with and without CO$_2$ (after Fine and Stolper)

Fig. 39. IR absorptance of CO$_2$ in Na$_2$O-Al$_2$O$_3$-SiO$_2$ glasses (Stolper et al.)
Mass Pyrograms Showing Release of CO$_2$ from CaO-MgO-SiO$_2$ Glass, Quenched from 20 Kbar and 1725°C (Rai et al., 1983)

**Fig. 40.** Pyrolysis of CaO-MgO-SiO$_2$ glasses containing CO$_2$ (Rai et al.)
NITROGEN IN SODA-LIME-SILICA GLASS, 1400°C, 2 HOURS
(Mulfinger)

Glass + 3 Wt. % C, Bubbled With N₂
Gas Furnace, Reducing Flame

Gas Furnace, Oxidizing Flame

Fig. 41. N in S-L-S glass, 2 hr at 1400°C (Mulfinger)
Fig. 5. Infrared spectra of soda-lime-silica glass. (Ia) After melting in gas furnace, (Ib) after bubbling with H$_2$O for 2.5 hr at 1400°C and $p_{H_2O}$ of 380 torr, (Ic) after bubbling parts of samples Ia and Ib with ammonia for 1.5 hr at 1400°C; spectra for these samples were identical.

Fig. 42. IR absorptance of N in S-L-S glass (Mulfinger)
Infrared spectrum of soda-lime-silica glass + 5 wt.
Si₃N₄ after melting for 17 hr at 1400°C.

Fig. 43. Removal of H₂O from glass by chemical dissolution
of N₂ (Mulfinger)
Nitrogen Solubility in Soda-Silica Glasses vs Silica Content and Equilibration Temperature (Swarts, 1970)

Fig. 44. N₂ solubility vs T and SiO₂ content in Na₂O-SiO₂ glasses (Swarts)
Nitride, $N^{-3}$, Dissolved in CaO-MgO-SiO$_2$ Glasses
(after Martinez and Sano, 1990)

**Fig. 45.** $N_2$ dissolved as $N^{-3}$ in CaO-MgO-SiO$_2$ slags
(Martinez and Sano)
Sulfur Content of Soda-Silica Glasses vs O₂ Partial Pressure (after Nagashima and Katsura, 1973)

Dashed line – 1250°C
Solid line – 1300°C

Fig. 46. S in Na₂O-SiO₂ glasses (Nagashima and Katsura)
Raman Spectra of Alkali-Silicate Glasses Containing Dissolved Sulfate (after Konijnendijk and Buster, 1977)

a) $\text{K}_2\text{O}-\text{SiO}_2$

b) $\text{K}_2\text{O}-\text{SiO}_2 + \text{K}_2\text{SO}_4$

c) $\text{Na}_2\text{O}-\text{SiO}_2 + \text{Na}_2\text{SO}_4$

Fig. 47. Raman spectra of $\text{SO}_4^{2-}$ in glass (Konijnendijk and Buster)
FIG. 86 — Curve of spectral transmission of Na$_2$O . CaO . 6 SiO$_2$ glass (1) with 2% of Fe$_2$O$_3$ under strongly oxidizing conditions, (2) with 2% under strongly reducing conditions; the sample was 2 mm thick [1.27].

Fig. 48. Fe$^{+2}$ and Fe$^{+3}$ spectra in glass
Fig. 2.1. Linear absorption coefficients of ferrous and ferric iron.

Fig. 49. Extinction coefficients for Fe$^{+2}$ and Fe$^{+3}$ in glass
EVOLVED GAS DETECTION

Stelzner et al. (1988)

* Evolved gas vs temperature
* Mass spectrometric analysis
* Assignments of physically and chemically dissolved oxygen

![Graph showing evolved gas vs temperature](image)

**Fig. 50.** Extraction of physical and chemical O₂ from glass (Stelzner et al.)
Table II. Measured Values of the Solubility Constant S (in $10^{-3}$kg/m$^3$) for Various Gases in Soda-Lime-Silica Glasses

<table>
<thead>
<tr>
<th></th>
<th>1000°C</th>
<th>1200°C</th>
<th>1400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.59</td>
<td>0.59</td>
<td>0.63</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>2200</td>
<td>2500</td>
<td>2700</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>O$_2$</td>
<td></td>
<td></td>
<td>1280</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>340</td>
<td>230</td>
<td>170</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>$4.7 \cdot 10^7$</td>
<td>$4.5 \cdot 10^5$</td>
<td>$1.3 \cdot 10^4$</td>
</tr>
</tbody>
</table>

Fig. 51. Solubility constants of gases dissolved in S-L-S glasses (Krämer)
### Concentrations of Dissolved Gases in Commercial Glasses, Typical

<table>
<thead>
<tr>
<th>Values</th>
<th>10^4 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>80–280</td>
</tr>
<tr>
<td>N₂</td>
<td>0.2</td>
</tr>
<tr>
<td>O₂</td>
<td>40–160</td>
</tr>
<tr>
<td>CO₂</td>
<td>60–80</td>
</tr>
<tr>
<td>SO₂</td>
<td>2500</td>
</tr>
</tbody>
</table>

*Fig. 52. Concentrations of gases dissolved in commercial compositions (Krämer)*
Fig. 53  Temperature Coefficients of Solubility
<table>
<thead>
<tr>
<th></th>
<th>1000°C</th>
<th>1200°C</th>
<th>1400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>115</td>
<td>164</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.07</td>
<td>0.5</td>
<td>2.1</td>
</tr>
<tr>
<td>N₂</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>O₂</td>
<td>0.038</td>
<td>0.64</td>
<td>5.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.07</td>
<td>1.4</td>
<td>10.5</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.03</td>
<td>0.13</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Fig. 54. Diffusion constants of gases in S-L-S glasses (Krämer)
Dissolution of helium bubbles at different temperatures

Fig. 55. Shrinkage of He bubbles in molten glass (Frischat)
Physical dissolution of Ar and N₂ in Float Glass: Diffusion of those Gases from Glass into O₂ Bubbles (Swarts)

Note:
Ar/N₂ in air = 0.012

van der Waals diameters:
N₂ = 2.86Å
Ar = 3.14Å

<table>
<thead>
<tr>
<th>Anodic O₂ bubbles in glass as melted</th>
<th>Partial Pressures in Analyzed Bubbles, Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial #1, 0.5 hr electrolysis</td>
<td>O₂</td>
</tr>
<tr>
<td></td>
<td>(major) 0.15</td>
</tr>
<tr>
<td>Trial #2, 5 hr electrolysis</td>
<td>(major) 0.07</td>
</tr>
</tbody>
</table>

**Conclusion:** Ar/N₂ ratio in bubbles, 0.02, was of the same order of magnitude as in air, 0.01

After glass was bubbled (equilibrated) with N₂ for 1.5 hr, then alternately electrolyzed and refined to remove all N₂ bubbles

<table>
<thead>
<tr>
<th>Anodic O₂ bubbles in glass as melted</th>
<th>Partial Pressures in Analyzed Bubbles, Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O₂</td>
</tr>
<tr>
<td>(major)</td>
<td>0.43</td>
</tr>
</tbody>
</table>

**Conclusion:** Since Ar/N₂ ratio was an order of magnitude smaller than in the original glass, equilibrating with N₂ dissolved more in the glass.

After glass was bubbled (equilibrated) with Ar for 1.5 hr, then alternatively electrolyzed and refined to remove all Ar bubbles

<table>
<thead>
<tr>
<th>Anodic O₂ bubbles in glass as melted</th>
<th>Partial Pressures in Analyzed Bubbles, Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O₂</td>
</tr>
<tr>
<td>(major)</td>
<td>0.36</td>
</tr>
</tbody>
</table>

**Conclusion:** Since the Ar/N₂ ratio in the anodic bubbles was orders of magnitude larger than before, much more Ar had been dissolved in the glass

Fig. 56. Detection of physically dissolved N₂ and Ar dissolved in float glass equilibrated with air (Swarts)
Fig. 57. Flows toward the spring-zone.
<table>
<thead>
<tr>
<th>Surface</th>
<th>446</th>
</tr>
</thead>
<tbody>
<tr>
<td>8&quot;</td>
<td>1032</td>
</tr>
<tr>
<td>16&quot;</td>
<td>1354</td>
</tr>
<tr>
<td>24&quot;</td>
<td>1165</td>
</tr>
<tr>
<td>32&quot;</td>
<td>1406</td>
</tr>
<tr>
<td>40&quot;</td>
<td>N.S.1</td>
</tr>
</tbody>
</table>

Fig. 58. Typical bubble concentrations uptank of the spring-zone of a large float tank.
N₂ and CO₂ in Bubbles from the Melter of a Float Glass tank

<table>
<thead>
<tr>
<th>Depth</th>
<th>N₂ / CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>8.1%</td>
</tr>
<tr>
<td>8&quot;</td>
<td>8.5%</td>
</tr>
<tr>
<td>24&quot;</td>
<td>4.3%</td>
</tr>
<tr>
<td>32&quot;</td>
<td>2.2%</td>
</tr>
</tbody>
</table>

Fig. 59. Gas analyses, bubbles from dip samples
**BUBBLES IN A SIEMENS FLOAT TANK**

<table>
<thead>
<tr>
<th>Depth</th>
<th>Bubbles/cm³</th>
<th>Diameter, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>15</td>
<td>0.15 - 0.40</td>
</tr>
<tr>
<td>10&quot;</td>
<td>28</td>
<td>0.02 - 0.30</td>
</tr>
<tr>
<td>20&quot;</td>
<td>47</td>
<td>0.02 - 0.30</td>
</tr>
<tr>
<td>28&quot;</td>
<td>47</td>
<td>0.02 - 0.25</td>
</tr>
<tr>
<td>40&quot;</td>
<td>40</td>
<td>0.02 - 0.30</td>
</tr>
<tr>
<td>43&quot;</td>
<td>56</td>
<td>0.02 - 0.25</td>
</tr>
</tbody>
</table>

*In the ribbon - 5-6 orders of magnitude fewer bubbles!*

*Bubble composition - 80-100% CO₂, balance N₂*

*Fig. 60. Enlargement of bubbles by sulfate refining*
Change in composition of an Oxygen Bubble

Fig. 61. Interdiffusion of gases between bubble and melt
Fig. 1. Photomicrograph of large defect bubble containing (a) liquid condensate and (b) fixed deposit.

Fig. 62. Deposits in bubbles from float glass
Fig. 2. Scanning electron micrograph showing interior surface of defect bubble containing (a) condensate and (b) fixed deposit.
Gas Analyses (Average values) of Bubbles from the melter of a Float Tank

<table>
<thead>
<tr>
<th>Location</th>
<th>N₂</th>
<th>CO₂</th>
<th>COS</th>
<th>S₂*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>1.5</td>
<td>18</td>
<td>0.6</td>
<td>(211)</td>
</tr>
<tr>
<td>8&quot;</td>
<td>3.7</td>
<td>40</td>
<td>3.6</td>
<td>(184)</td>
</tr>
<tr>
<td>24&quot;</td>
<td>8.0</td>
<td>152</td>
<td>35</td>
<td>(36)</td>
</tr>
<tr>
<td>32&quot;</td>
<td>4.8</td>
<td>210</td>
<td>5.7</td>
<td>(10)</td>
</tr>
</tbody>
</table>

* These are vapor pressure values calculated for the S₂ vapor assumed present in the bubble before it condensed upon cooling of the glass to room temperature. These values were calculated from an assumed total pressure of about 230 torr in the bubble at room temperature and subtraction of the measured pressures of the non-condensed species.

Conclusion: In the melter, these bubble contained sulfur vapor as the principal gaseous species, rather than SO₂ as commonly suggested.

Fig. 64. Calculated partial pressures of elemental S° present in bubbles from float glass dip samples
Fig. 65. Exchange of gases between bubble and melt, O₂-fined TV glass (Krämer)
Variation de la concentration en azote dissous en fonction des différentes zones d'un four en action.

Fig. 66. Dissolved N₂ vs location in glass from a container tank (Debras et al.)
Evolution des pourcentages en azote présent dans des bulles en fonction des concentrations en azote dissous dans la masse.

Fig. 67. Correlation of dissolved N₂ with N₂ in bubbles taken from same locations (Debras et al.)
Relation between diameter of a bubble and its equilibrium internal pressure assuming a surface tension of 300 dyne cm\(^{-1}\) (ref. 54).

Fig. 68. Pressure increase within a bubble due to surface tension
Fig. 69. Schematic representation of scale and intensity of segregation in a binary mechanical mixture (ref. 75).
Striagrams of plate glass having different levels of internal inhomogeneity.

Fig. 70. Striagrams of plate glass
Different levels of inhomogeneity in plate glass as seen by striagram and by interferometry.

Fig. 71. Use of chemical etching and interferometry
Fig. 72. Schematic representation of reduction of concentration differences by diffusion (Cooper)
Fig. 73. Reduction of heterogeneity by attenuation and diffusion
Fig. 74. Fe$^{3+}$/Fe$^{2+}$ vs P$_{02}$ (Johnston)
Fig. 75. Redox ratios of multivalent ions vs P_{O2} (Shreiber)
Fig. 76. Temperature dependence of equilibrium constants (Johnston)
Fig. 77. Equilibration of commercial float glasses in air
Fig. 78. Temperature dependence of redox ratio in commercial float glass
Indication of how the upper state is favoured in the Fe$^{2+}$/Fe$^{3+}$ equilibrium in $M_2O$-SiO$_2$ systems by (i) increasing alkali oxide content and (ii) changing from lithium to sodium to potassium for given mol% of alkali oxide. Redox data are from Reference 5.

Fig. 79. Redox ratio vs basicity (Baucke and Duffy)
Fig. 80. Redox ratios for Sn and Fe (Johnston)
<table>
<thead>
<tr>
<th>Redox couple</th>
<th>( E_m ) (Melt, ( T^\circ C ))</th>
<th>( E^0 ) (Aqueous, ( 25^\circ C ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SRL-131 1150</td>
<td>FAS 1500</td>
</tr>
<tr>
<td>b Ni:3-2</td>
<td>1.7 1.5</td>
<td>1.75</td>
</tr>
<tr>
<td>a Co:3-2</td>
<td>1.4 1.1</td>
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</tr>
<tr>
<td>e Au:3-0</td>
<td>&gt;0.8</td>
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<tr>
<td>c Mn:3-2</td>
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<tr>
<td>i Ag:1-0</td>
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<td>0.80</td>
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<tr>
<td>f O:O(_2)-2-</td>
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<tr>
<td>d Ce:4-3</td>
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<td>h V:5-4</td>
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<td>-2.7 1.00</td>
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<tr>
<td>x Cr:3-2</td>
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<td>o Mo:6-5</td>
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<td>t Ti:4-3</td>
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Reference: Johnston [1965], Milazzo and Caroli [1978]

Fig. 81. An electromotive series for ions in glass (Schreiber)
Fig. 82. Comparison of electromotive series for glass and H₂O
Fig. (1) Theoretical square-wave voltammogram of a one-electron-step at 1100°C

Fig. (2) Experimental square-wave voltammogram of an iron doped soda-lime-silica glass melt (0.5 mol-% Fe₂O₃, θ = 1100°C)

Fig. 83. Theoretical and experimental voltammograms (Rüssel)
Square-wave voltammogram of a glass melt doped with Sb$_2$O$_5$
(1 mol-% Sb$_2$O$_5$; $\theta = 900^\circ$C; $\tau = 10$ ms, $\Delta E = 100$ mV)

Fig. 84. Voltammogram for the two-step reduction of Sb$^{5+}$
(Rüssel)
Fig. 85. Schematic of undercutting at a side-wall
Fig. 86. Schematic of upward drilling
Elevation view of a continuous glass-melting furnace

Fig. 87. Schematic of viscous refractory-reaction glass in the bottom of a Siemens melter
Fig. 88. Schematic of refractory-reaction glass in a submerged throat tank
Fig. 89. Sketch of lab equilibration of bonded AZS/glass and generation of bubbles
The Glasstech Mixmelter for waste vitrification: the impeller and the furnace lining, both made of refractory metal, are used as power electrodes

Fig. 90. The proposed Glasstech Mixmelter (Richards, figure from Barton)
Fig. 91. "Scull-melter" concept
Figure 8. Battelle's Pyroflux glass melter in which the sand, feldspar, lime and dolomite are preheated with a cyclone cascade.

Fig. 92. Battelle Pyroflux melter (figure from Barton)
RAMAR (rapid melting and refining). Owens Illinois.

Fig. 93. O-I RAMAR (figure from Barton)
Fig. 94. O-I RAMAR, perspective sketch
PPG melting and refining system (200 t/day). Not to scale (assembly of patent diagrams)

Fig. 95. Schematic of the PPG new process
AGM (advanced glass melter). Gas Research Institute.

Fig. 96. Schematic of GRI's AGM (figure from Barton)
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