Glass Processing

Lecture #17. Silica Glass Processing Part 1

Thomas P. Seward III
Corning Incorporated (retired)
Alfred University (retired)
(TPSConsulting@stny.rr.com)

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Outline

Day One

1. Introduction - Silica Glass (SiO_2) - Its technological importance (Properties, Applications) – Its manufacturing difficulties
2. Innovations in manufacturing history
3. Type classifications for transparent silica glass
4. Silica glass from natural raw materials

   Processes and resulting characteristics

Day Two

1. Synthetic fused silica manufacturing

   Processes and resulting characteristics

   Deliberate addition of modifying chemical species.
2. Modern Applications

   Examples -Telescope mirrors, microlithography optics, optical fiber
3. Summary and Acknowledgements

A Unique Material

- Silica glass is a quite unique material.
- It is the only single-oxide glass former that is widely used on its own (not having its chemical composition highly modified).
- It has properties unlike any other material.
- These properties are in demand for many applications, some of them high-tech. Or at least essential to manufacturing high-tech products.
- Let's look at come of these properties.

Fused Silica Characteristics

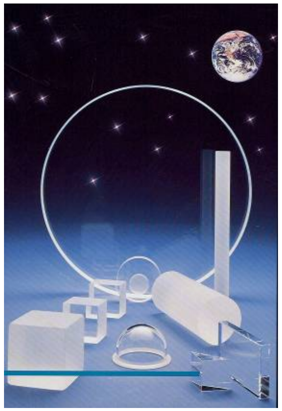
- Low thermal expansion

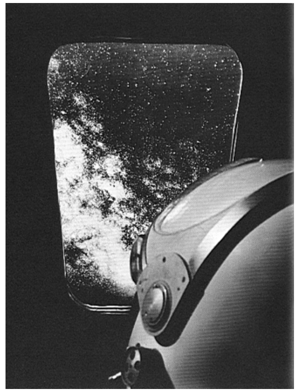
  (0 to 300 ºC) about 0.55 ppm/ºC or 5.5 x 10^{-7}/ºC
- High thermal shock resistance
- Refractory – High viscosity and high use temperatures

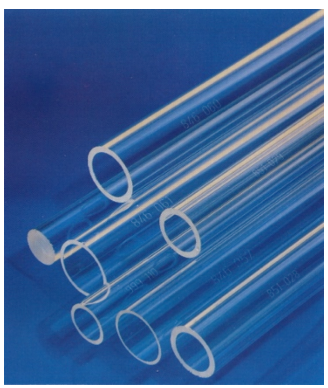
  Viscosity about 10^7 poise at 1700˚C

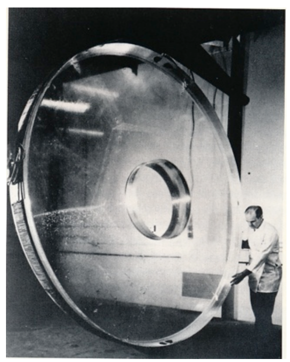
  Softening point generally above 1550 ˚C)
- High optical transparency; wide transmission band (DUV- near IR)
- Excellent chemical durability
- Good radiation damage resistance
- High electrical resistivity, low dielectric constant and low loss tangent.

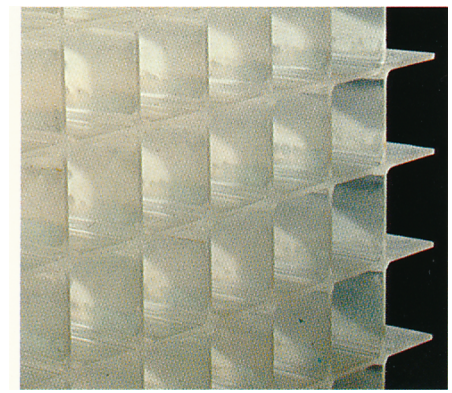
Fused Silica Applications

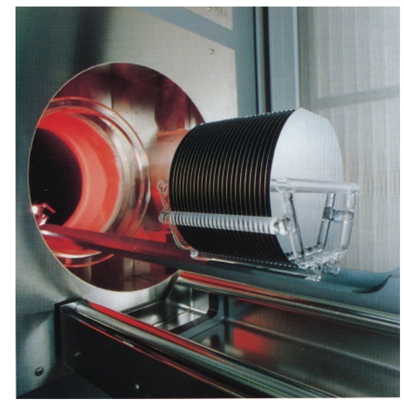












Key properties: Excellent optical transparency, low thermal expansion, high use temperature, low electrical conductivity, low alkali content,

Manufacturers' Product Literature

Important Fused Silica Applications

- Because of silica's almost unique combination of characteristics, it is used for many different specialized applications:
  - Lighting (high-intensity-discharge, quartz-halogen, and uv lamp envelopes)
  - Semiconductor industry manufacturing (crucibles, furnace tubes, substrates, microlithography optics)
  - Optical elements (lenses, windows, mirrors) including high energy laser optics
  - Optical fiber and photonic devices
  - Astronomical telescope mirrors
  - Space craft windows
  - Other (including labware, tubing, specialty fiber and wool-type fiberglass).

Group Applications by Property

- Refractory
  - High temperature lamp envelopes
  - Spacecraft windows
  - Crucibles and furnace refractories
- High optical transparency
  - UV optics
  - Optical fiber for telecommunications
- Low thermal expansion
  - High temperature lamp envelopes
  - Spacecraft windows
  - Thermally stable mirrors (astronomical telescopes, IC microlithography stepper camera optics)
- High purity
  - IC microlithography stepper camera optics

Available in a Variety of Forms

- Powders
- Coatings
- Thin films
- Fibers
- Porous bodies
- Bulk glass
  - Translucent
  - Transparent

This and the following lecture will concentrate primarily on bulk transparent glasses.

Nomenclature

- Commonly used names:
  - Silica glass (but sometimes this name is used for all silicate glasses)
  - Vitreous silica
  - Fused quartz, quartz glass, and sometimes just "quartz" (sometimes reserved for when natural quartz or rock crystal is the raw material)
  - Fused silica (at one time only used when sand was the raw material)
  - Synthetic fused silica, synthetic quartz, synthetic quartz glass (when made from synthetic raw materials such as silicon tetracloride and siloxanes)

- Frequently all but the last are used interchangeably.

Intrinsic vs. Extrinsic Behavior

Transport properties (e.g. viscosity and electrical conductivity) are very dependent on purity and manufacturing method through:

- water content (H_20)
- impurity content (other than H_20)
- thermal and/or manufacturing history

The intrinsic capabilities of silica may never have been measured.

Table 7. Viscosity Data[a]

Parameter	Quartz Syndicate, Inc. Transparent	Quartz Syndicate, Inc. Translucent	G.E.-204	Vitreosil ir	Vitreosil OG[b]	Heraeus Supersil	Corning 7940	Dynasil
silica type	I	I	II	II	I	III	III	III
OH, ppm			low	3	400	1200	900–1000	600–1000
softening point, °C	1670	1650	1813	1582	1597	1600	1585	1600 ± 25
annealing point, °C	1140	1100	1213	1190	1108	1075	1075	1100 ± 20
strain point, °C	1070	1040	1107	1108	1015	987	990	1000 ± 20

[a] Data from manufacturers' product literature; data for Vitreosil from Ref. 134.
[b] OG = optical grade.

From Encyclopedia of Chemical Technology, 1994

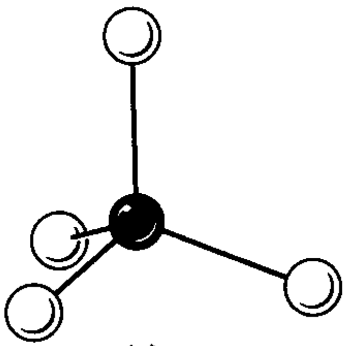
Properties Affected by Purity

Two Examples

Viscosity
Near Infrared Absorption

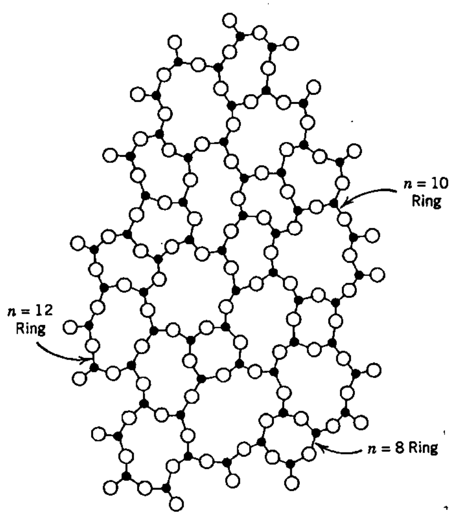
Silica Glass and Liquid Structure

The basic building block of all condensed phases of silica (liquid, crystal or glass) is the SiO_4 tetrahedron.



(a)

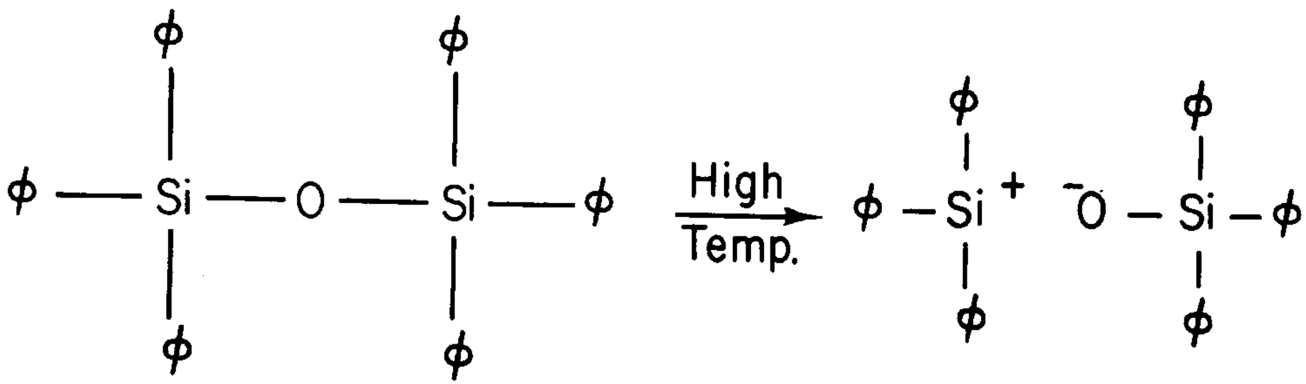
In the liquid or glass states, these tetrahedra are bonded together through shared oxygens to make a continuous structure.



One may ask, if all the tetrahedra are bonded to each other, how can the liquid flow? Or, how does the solid glass soften when heated?

Good questions!

Viscous Flow of Silica



- For flow, broken bonds must be present.
- Thermal energy tends to break bonds.
- With increasing temperature, progessively more bonds are broken.
- The more broken bonds, the more easily the glass flows (viscosity decreases).

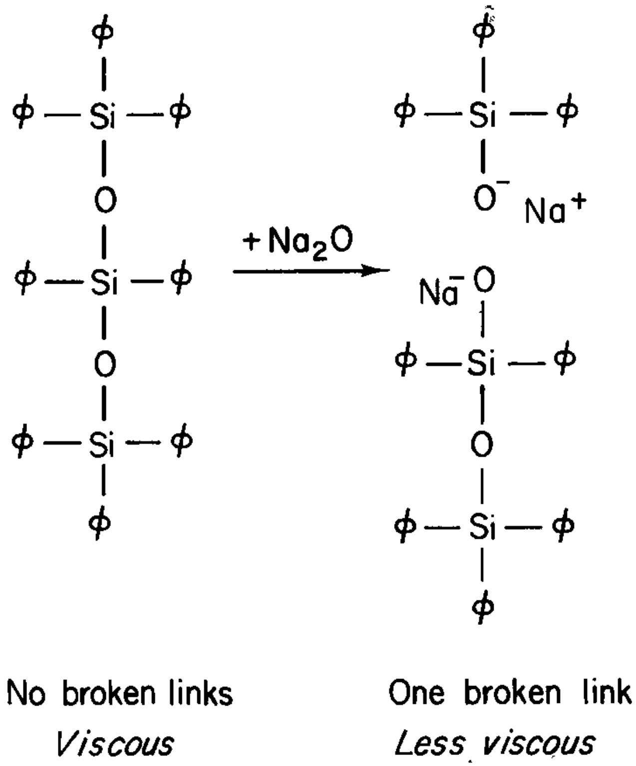
Effect of Impurities/Modifiers on Viscosity

Other factors can provide broken bonds.

For example, each molecule of soda (sodium oxide) added creates one NBO (non-bridging oxygen).

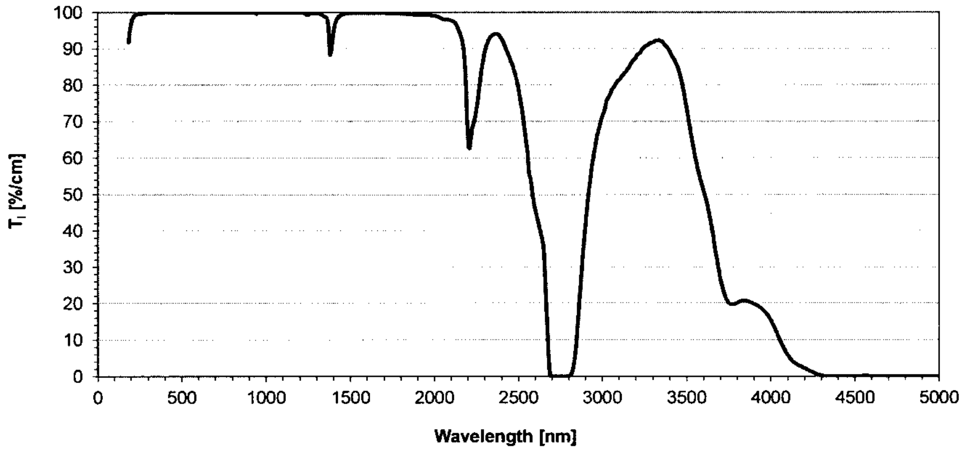
Other modifiers have a similar effect. For example, H_2O.

It makes sense that the more modifiers present, the more easily the glass flows.

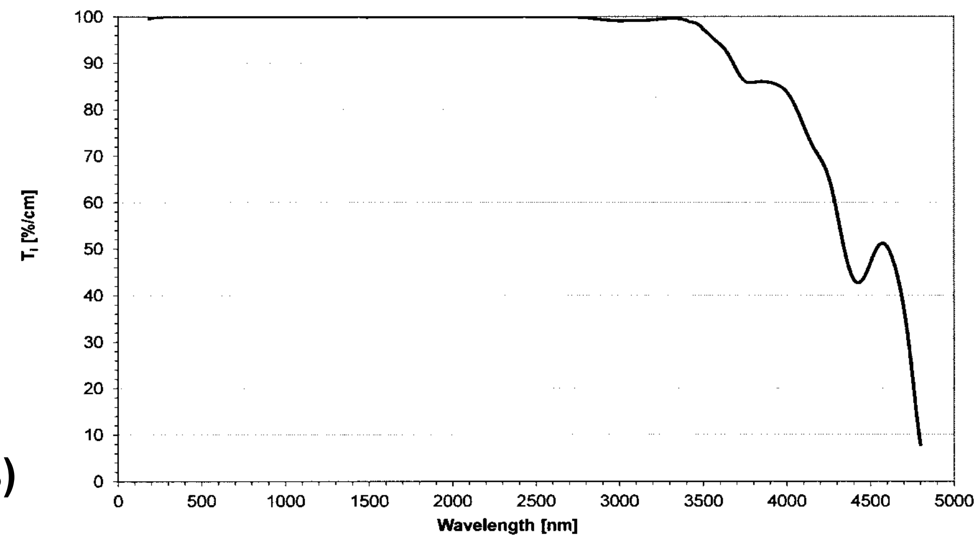


Effect of Dissolved H_2O on IR Transmission

Corning Code 7980
Type III
800-1000 ppm OH



Corning Code 7979
Type IV
< 1 ppm OH



Internal Transmittance
(corrected for reflection losses)

Key Point So Far

- Important properties of silica glass depend on its degree of purity.
- Impurities include – metal oxides, other glass-forming oxides, dissolved gases (including hydrogen, chlorine, and H_2O).
- Purity in turn depends on the starting raw materials (chemical sources) and the manufacturing process.
- The ultimate properties of "absolutely" pure fused silica have never been measured.

- We will look at how raw materials and processes produce subtle, and sometimes not so subtle, variations in properties.

- The processes themselves are generally expensive and so are the products.

Exercise

- We just saw examples of how impurities such as water and alkali oxides can affect viscosity and optical transmittance of silica glass.

- Think of some other properties of silica glass and how different impurities might or might not affect them.

Note: This exercise and others to follow are not for class discussion, but could be considered as useful homework.

Manufacturing Processes

Modern Processes

- We will see that all modern process for manufacturing bulk silica glass involve the preparation and viscous sintering of small, amorphous (glassy) silica particles.

- How this viscous sintering is accomplished, effects the purity and homogeneity, both chemical and structural.

- Variables including the size and composition of the starting particles and the method used for sintering.

Raw Materials and Heat Sources

- The starting materials are primarily of two types
  - Crystalline quartz of varying purity from natural quartz deposits (in places like Brazil and Madagascar) or high quality glass makers sand (for example from Pennsylvania and West Virginia)
  - Liquid compounds, both inorganic and organic, e.g., halides, siloxanes, and teraethylorthosilicate (TEOS)

- The heat sources also are primarily of two types
  - Electrical – electric arcs, resistance and induction heaters, and high frequency plasma discharges
  - Chemical combustion – hydrogen-oxygen and natural gas-oxygen burner flames (Natural gas is primarily methane.)

Crystalline Forms of Silica

- Stability ranges:

Cristobalite	1470 - 1723 °C
Trydamite	870 - 1470 °C
Quartz	below 870 °C

Low quartz to high quartz phase transition at 573 °C

- On heating, quartz transforms to cristobalite before it melts
- T > 1730 °C required to form an all-liquid melt

- Boiling point 2300 °C

Viscosity – Temperature Relationships

- Different glass compositions can have dramatically different temperature dependences.
  - 0080 is a soda-lime-silica glass.
  - 7740 is original Pyrex
  - 1720 is an aluminosilicate glass.
- Orange indicates viscosities needed for batch melting and fining in traditional glass furnaces.
- Silica is way off-scale!

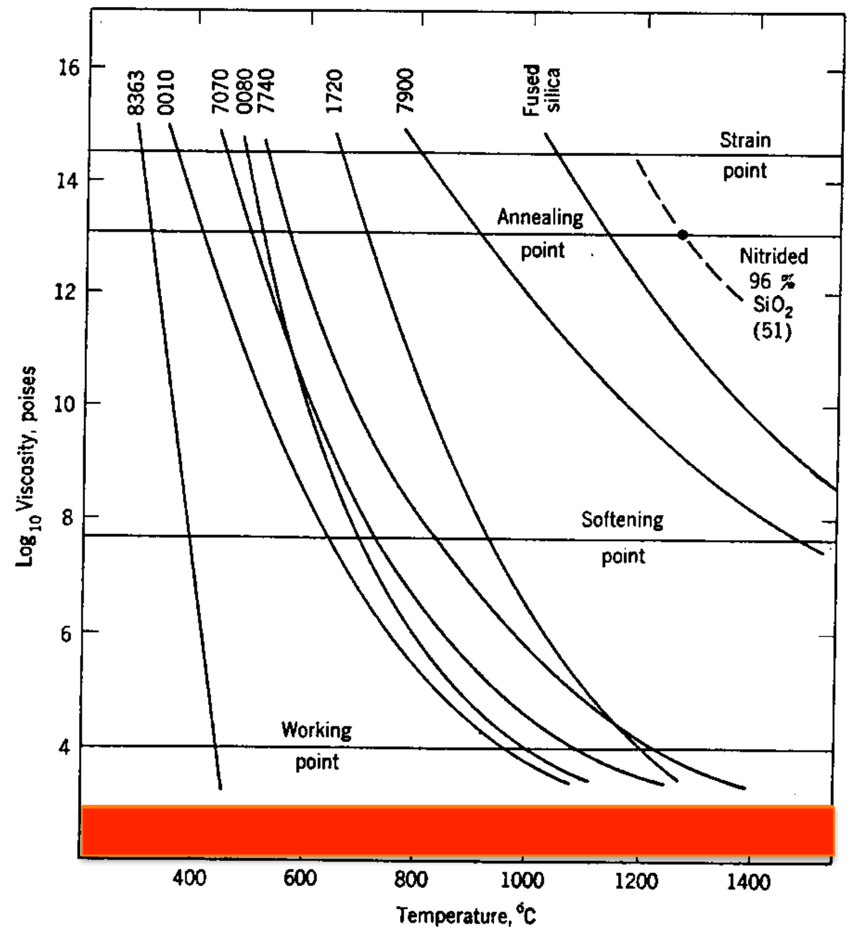


Fig. 19. Viscosity vs temperature for some commercial glasses. Courtesy Corning Glass Works.

Manufacturing Challenges

- The refractoriness poses major melting difficulties
  - The high temperature crystalline phase (cristobalite) melts at about 1725 °C.
  - The viscosity at that temperature is about 10^7 poise.
  - This rules out conventional melting techniques.

- Silica melts tend to react with their containers. For example
  - $SiO_2 + C \rightarrow SiO\ (gas) + CO\ (gas)$

- At high temperatures SiO_2 is noticeably volatile. The boiling point is only 2,300 °C.

- The manufacturing processes often introduce chemical impurities, including dissolved water and halogen gases, but high chemical purity (50-100 ppb impurities) is often required by applications.

Effect of Melting Atmosphere

- During glass melting processes, molten glass tends toward chemical equilibrium (to varying degrees) with the furnace atmosphere.
- Some atmospheric gases dissolve into the glass changing its properties.
- Example gases: Cl_2, CO_2, H_2O
- This is true when processing SiO_2 as well as when processing more traditional glasses.

Effect of Furnace Atmosphere on Glass Composition

- Electric furnace
  - Air approx. 80% N_2 and 20% O_2, a relatively dry, oxidizing environment
- Gas-air fired furnace
  - Lots of N_2 from the air, lots of the combustion products CO_2 and H_2O, and probably some O_2, depending on how the burners are adjusted.
- Gas-oxygen fired furnace
  - Little N_2, so mostly CO_2, H_2O and some O_2, depending on how burners are adjusted. If the gas is H_2, then little CO_2 produced.
- Effects:
  - Electric furnaces tend to be more oxidizing and introduce little H_2O.
  - Glass made in gas-oxy furnaces tend to contain a higher concentration of H_2O (1,000 ppm or greater).

Manufacturing Objectives

- First, find or develop a method for melting or otherwise making good quality transparent pieces of glass of a size appropriate to the application.
- Second, make the glass of sufficient purity and homogeneity to meet the requirements of the application.
- With silica these are difficult objectives. To achieve them is relatively expensive.

Early Processing History

Innovation Pre-20th Century

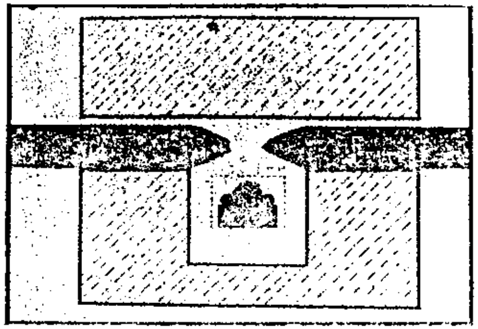
- 19th century - introduction of oxygen-injected or oxygen/fuel (as opposed to air/fuel) burners and torches allowed sufficient energy concentrations to melt crystalline quartz (> 1725 ºC); also lampworking with H_2-O_2 flame (including capillaries, bulbs and drawn fiber).
- Some dates
  - 1813 - First recorded melting of small quartz crystals with O_2 injected alcohol burner
  - 1821 – Melting of quartz crystals and lampworking wit H_2/O_2 torch
  - 1887 - Drawn fiber (cross-bow technique)
  - 1878 – Lamp-worked capillaries and thermometer bulbs at the Paris Exhibition

Innovation in the Early 20th Century

- 1899-1910 - commercial development in England, France and Germany - key issues were purity and transparency – production generally limited to translucent and semi-transparent crucibles, fiber, rods and tubing.

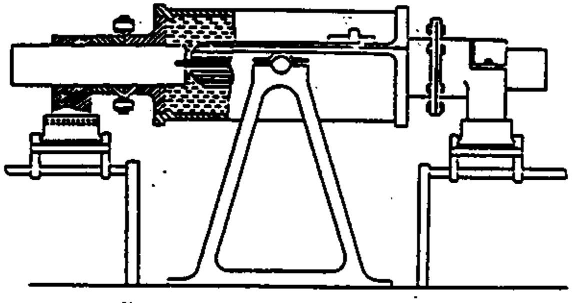
- Opaque materials called "fused silica" made by fusing sand with carbon arcs or resistively heated carbon electrodes Two examples:

Carbon Arc



Hutton - 1901

Carbon Resistance Heating



Bottomly, Hutton and Paget - 1904

Early 20th Century continued

- Tubing was sometimes made by drawing cane from a molten blob, then wrapping around a platinum rod and re-fusing.
- Transparent materials were made by melting clear, selected quartz crystals in an arc or flame and collecting them on a heated rod or surface below.
  - Arc Fusion
    - Shenstone and Kent, 1903
  - Flame Fusion
    - W.C. Heraeus, 1908
- These processes form the bases of modern technology and we will look at them further, but essentially they provide melts that form and solidify with the only solid contact being the glass that was previously formed. They are containerless process.

Innovation Mid 20th Century

- The beginnings of the modern era. This is where the processing part of the course really begins:

- Electric melting and flame fusion were further developed. Continuous drawing of rod and tubing from vertical electric furnaces became possible. Induction heating was introduced.

- Synthetic processes, in particular flame hydrolysis (1934) - U.S. patent by J.F. Hyde (Corning Glass Works) on flame hydrolysis of $SiCl_4$ issued in 1942; the basis for all synthetic fused silica processes used commercially today.

Manufacturers

- There are a great many (not a complete list)
- America
  - General Electric
  - Corning Incorporated
  - Osram Sylvania
  - Heraeus Amersil
  - Thermal American Fused Quartz
  - Dynasil Corp. of America (Russia)
- Germany
  - Heraeus Quarzschmelze
- France
  - Quartz et Silice
- England
  - Thermal Syndicate Ltd./Saint Gobain
- Japan
  - Toshiba Ceramics
  - Shin-Etsu
  - Tosoh./NSG

Transparent Silica Types

Table 1. Classification of Commercial Vitreous Silicas

Type	Method	Impurities, ppm			Uv cutoff[a], nm	Representative glasses
		OH	Cl	Cations		
I	electric melting of quartz	<20	0	50–300	220	Infrasil, Vitreosil-ir, GE-124, GE-214
II	flame fusion of quartz	200–500	0	10–50	210	Homosil, Optosil, Vitreosil-055
III	flame hydrolysis	600–1200	50–100	<1	170	Corning 7940, Dynasil 1000, Shinetsu P-10, Spectrosil, Suprasil, NSG-ES
IV	oxidation of $SiCl_4$ (plasma)	<20	<200	1–2	170	Spectrosil WF, Suprasil-W
V	sol–gel	<1	<1–500	<1	170	GELSIL

[a] Wavelength at which transmission drops to 50%.

From K-O Encyclopedia of Chemical Technology, 1994

Transparent Fused Silica Types

Chart to Assist Memory

	Electric Melting	Flame Fusion	
Natural Quartz	Type I	Type II	Less Pure
Synthetic Precursors	Type IV	Type III	More Pure
	Dry	Wet	

Exercise

- We have talked about how the high melting point of cristobalite (the most refractory crystalline form of silica) and the high viscosity of the melt at that temperature makes traditional glass melting methods impractical or impossible to use for silica.

- Considering what you already know about traditional glass <u>forming</u> processes, which of them do you think could or could not be applied to silica glass? Why or why not?

Electric Melting - Type I

Electric Melting of Quartz – Type 1

- Raw material
  - Source -traditionally crystalline quartz , the most pure being from Brazil and Madagascar
  - More recently, beneficiated high quality glassmaking sand
  - Multi-step preparation to purify and control grain size of both.
- Heat sources:
  - Electric arcs, resistance heaters or induction heaters
- Processes used extensively for the manufacture of crucibles, rod and tubing and objects made from them.

Vacuum and Pressure

- A major ongoing obstacle to optical clarity was the trapping of air between the quartz grains as they were melted and sintered together.
- Osram experimented with vacuum melting before WWII.
- General Electric pursued melting under vacuum before 1930 to remove the trapped air, then further consolidating the sintered mass under high pressure to minimize any remaining voids.
- The resulting mass of glass was called an ingot.
- Ingots could be further worked at high temperatures to produce many shapes.
- GE made telescope mirror blanks using this process by creating hexagonal shapes (6.5" and 22") and fusing them together in three layers. The one made for Kitt Peak in 1967 was 158" diameter. (This "hex-seal" process will be discussed further next week in conjunction with synthetic silica manufacturing.)

Electric Lighting Spurred Development

High pressure mercury arc introduced in 1934.

Necessitated high volume manufacture of silica glass tubing for arc chamber.

Lamp manufacturers lead the process development.

Heinlein (1939) is credited with the first commercial continuous process process.

Essentially a cold-crown, electrically heated vertical furnace with tubing drawn from an orifice at the bottom.

Many refinements since then.

General Electric Product Literature

Heinlein (Osram) Patent - 1939

- Continuous drawing of tubing or rod
- Tungsten filament heaters (m.p. 3,400 °C)
- Crucible, die (tapered orifice) and hollow mandrel made of molybdenum (m.p. 2,600 °C)
- Non-oxidizing atmosphere, e.g. nitrogen or forming gas (nitrogen/hydrogen mix)
- Crushed quartz fed in at the top, tubing pulled by rollers and belts below.

1. Crucible.
2. Tungsten heating elements.
3. Water-cooled cap.
4. Water-cooled cap.
5. Cylinder of pressed zirconia.
6. Water-cooled furnace jacket.
7. Cylindrical opening.
8. Mandrel.
9. Molybdenum tube.
10. Protective gas inlet to heating elements and crucible.
11. Charging shaft for quartz crystal.
12. Guide rollers.
13. Drawing bands.
14. Protective gas inlet to shaft (11).

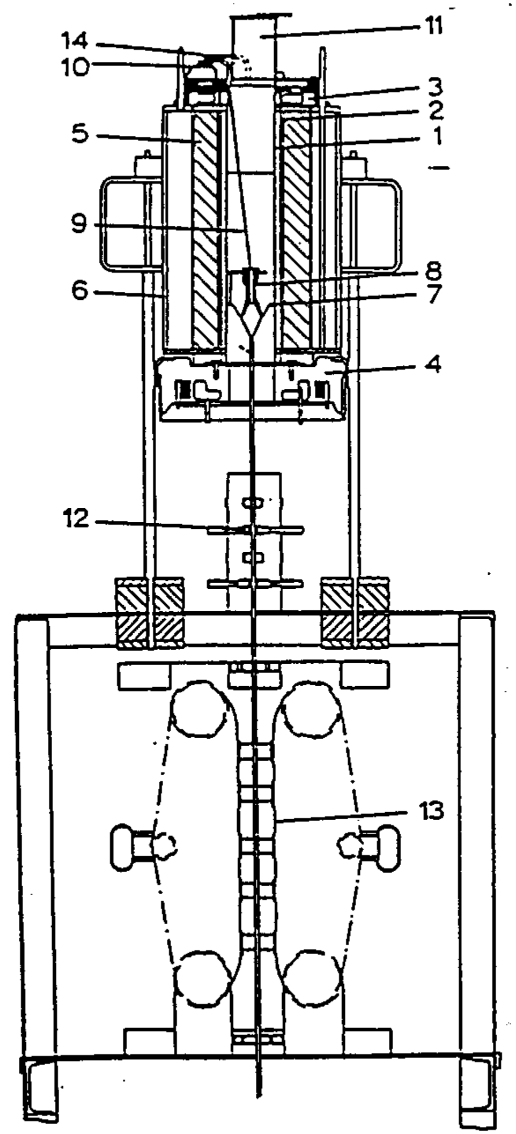


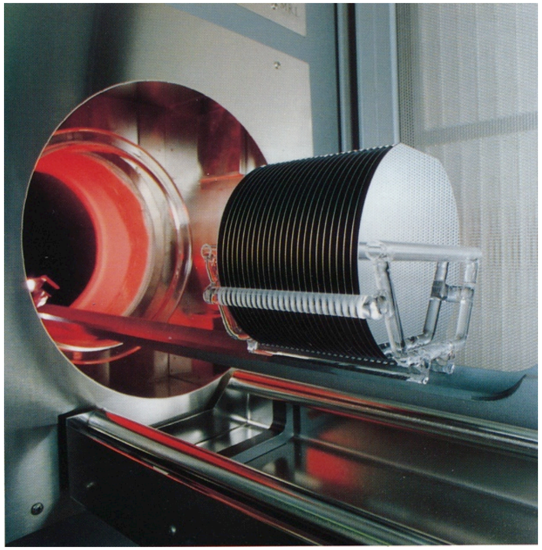
Figure 4. Hänlein Continuous Drawing Quartz Melting Furnace.

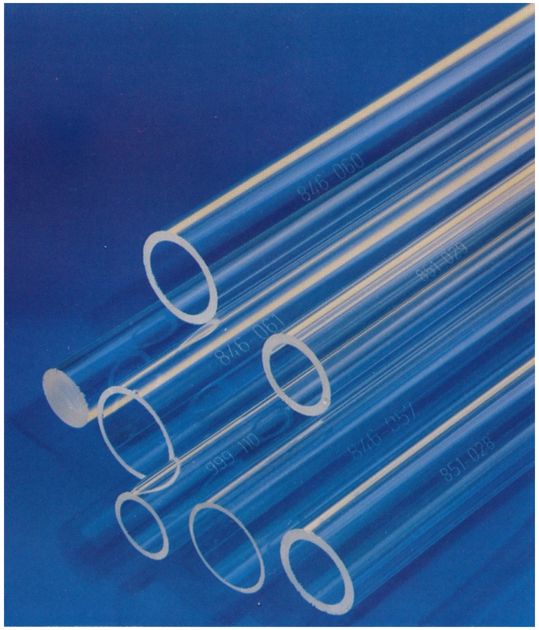
Variations

- Improvements and/or variations on the OSRAM process include:
  - Alternative refractory materials as insulation and for the glass contact materials
  - Replacing resistance heating with induction melting, which involves electromagnetically coupling the elecrical energy to the crucible which acts as a "susceptor."

Type I Tubing Applications

- Examples:
  - Electric lighting
  - Semiconductor (Integrated circuit) processing: rods, tubing, wafer carriers
  - Optical fiber substrate tubing (for the OVD/ MCVD process we will introduce next week).



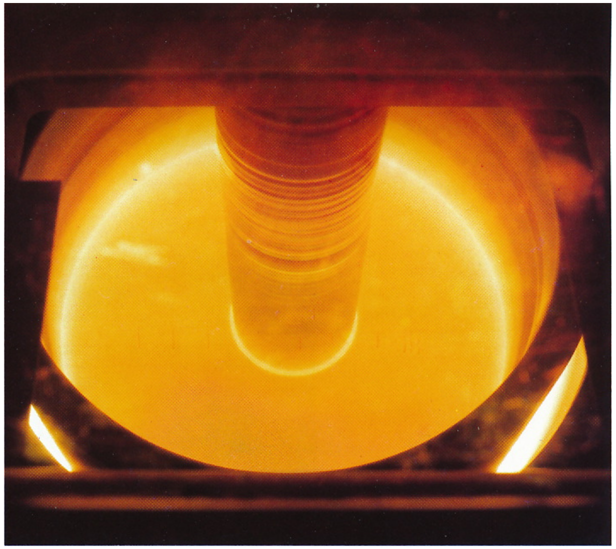


General Electric Product Literature

Electric Arc Fusion – Type I

While technically not considered Type I because they are not transparent, translucent crucibles made by electric arc fusion qualify in terms of their purity levels and method of manufacture.

They are an extremely important product used in many laboratory and commercial processes.



GE 500 Series "Quartz" Crucibles

General Electric Product Literature

Summary - Silica Glass - Type I

- Traditionally called "fused quartz" or just "quartz"
- Produced from natural quartz, sand, or beneficiated sand
- Electric fusion under vacuum or inert gas
- "Dry" - contains < 200 ppm OH (water)
- Some metallic impurities (e.g. < 200 ppm Al; < 400 ppm transition metals; < 50 ppm Na, but can be much less) – depends on the purity of the raw materials
- Examples:
  - Infrasil (Heraeus)
  - IR-Vitreosil (TSL)
  - General Electric 124, 214 standard lamp tubing & 224 low alkali (G.E.)

Flame Fusion – Type II

Flame Fusion of Quartz – Type II

- A direct outgrowth of Heraeus' 1908 innovation
- Essentially continuous deposition of molten granules of quartz or quartz sand onto a hot rotating mandrel where the granules sinter into a dense ingot or "boule" of glass.
- Chlorine gas can be introduced during the "laydown" of the glass to improve purity.
- Chlorine removes metal contaminants such as Al, Fe, Cu, Zn, Ti and the alkali and alkali-earth metals by forming volatile chlorides.
- Similarity to the Vernueil process for growing oxide crystals (1902), is shown on the next slide.

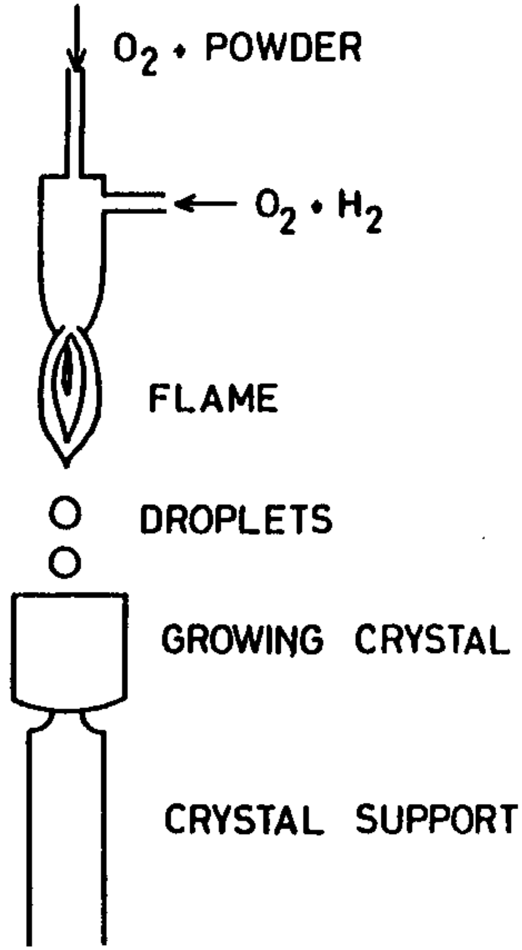
Vernueil Process

Originally developed for growing synthetic gemstones based on high melting point crystals such as alumina (m.p. 2072 °C). Examples: ruby and sapphire.

Crystalline powder melted in oxy-hydrogen flame.

Droplets land on seed crystal and crystallize in same orientation as seed.

The crystal mass is called a "boule."



Silica is an excellent glass former.

When molten quartz droplets settle on a substrate above about 1600 °C, they fuse together into a molten mass.

This mass does not crystallize at those temperatures nor when being cooled to room temperature.

The resulting mass of glass is also called a "boule."

Quartz Preparation

- Select highest purity raw material available
- Treat before melting to improve purity and reduce formation of gaseous inclusion during fusion
  - Wash in mixed acids to remove surface contaminants.
  - Heat to > 800 ^oC to cause micro-cracking from the from the high-low quarts transition.
  - Plunge into distilled water to enhance micro cracking.
  - Dry.
- Such powders are suitable for vacuum sintering as well as flame fusion, because they
  - Melt faster and
  - Release gaseous impurities more quickly

Heraeus Flame Fusion (Example)

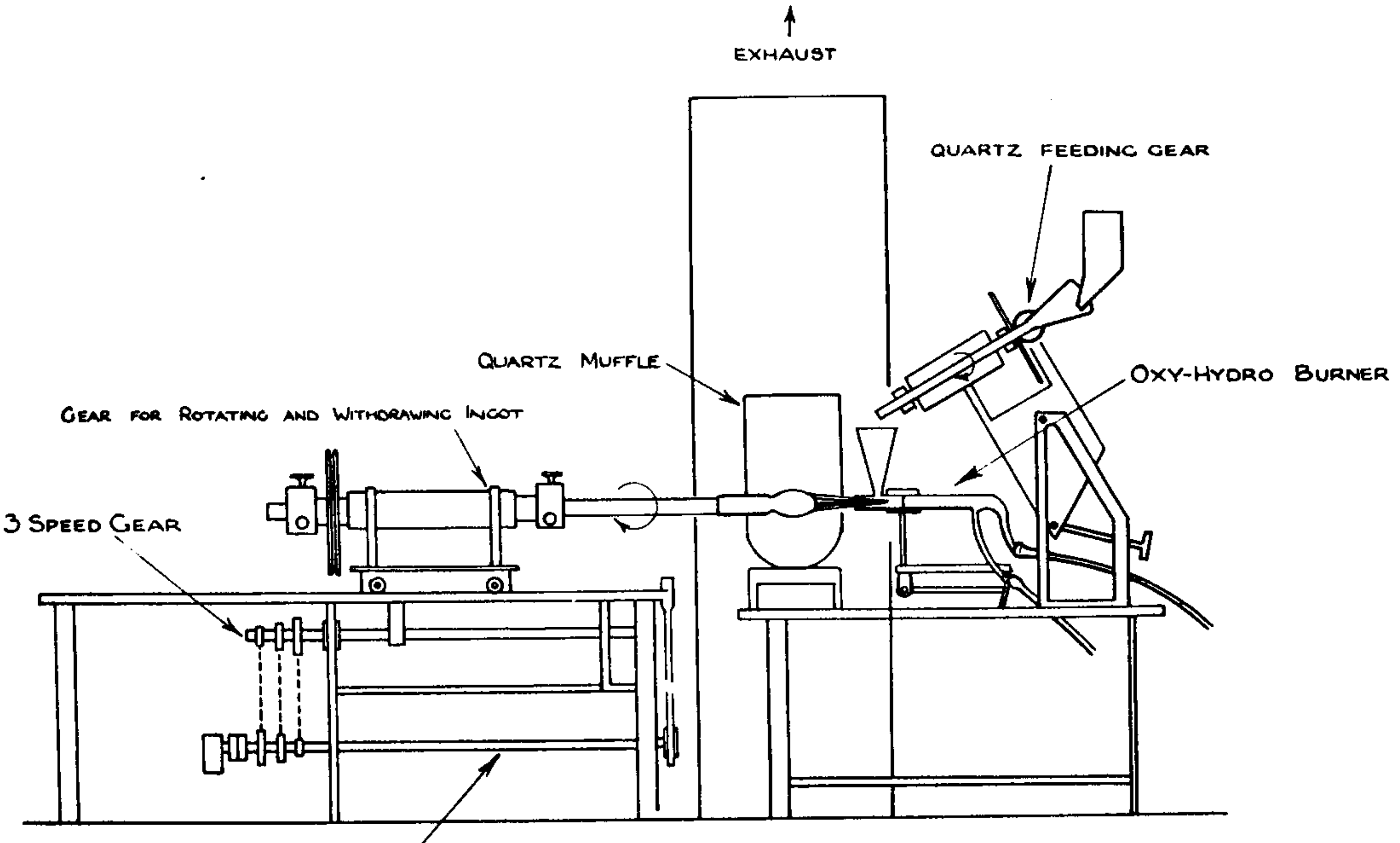


FIG. 2 HERREAUS QUARTZ MACHINE

From "Fused Quartz Manufacture in Germany," 1946

Heraeus Burner Detail

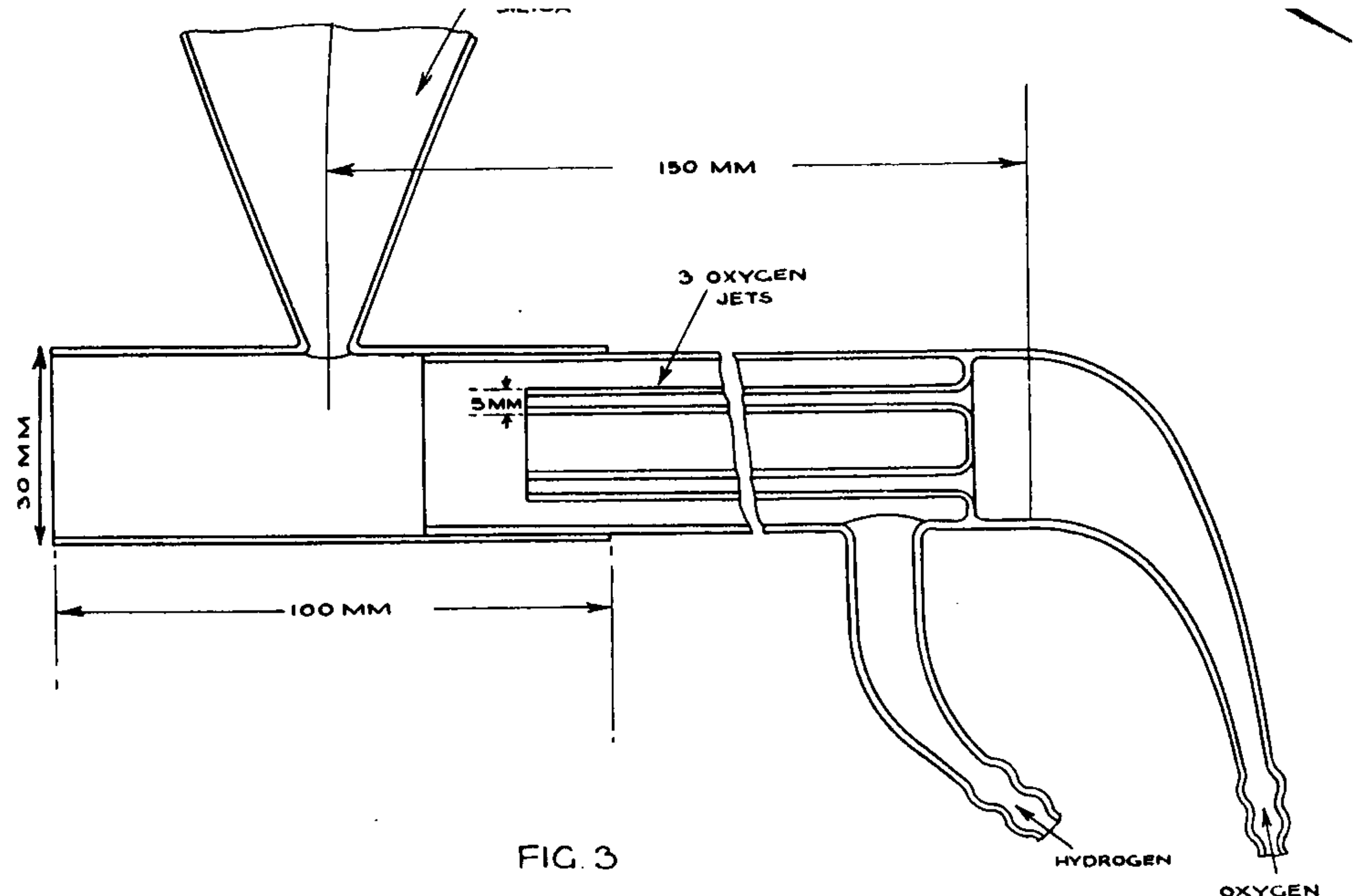


FIG. 3

HERREAUS BURNER FOR QUARTZ SPRAYING

SCALE – FULL SIZE MATERIAL – FUSED QUARTZ

From "Fused Quartz Manufacture in Germany," 1946

Flame Fusion on a Large Scale

- Pursued by General Electric
- Large slabs of fused silica (up to 6 feet) for telescope mirrors were generated by traversing the oxy-hydrogen torch, with granular quartz injected, across the slab, gradually building the thickness layer by layer.
- Major achievement was the prototype of a 200 inch telescope mirror for the Mount Palomar mirror. GE lost out to Corning Glass Works' cast borosilicate mirror because of cost and manufacturing difficulties.

Summary - Silica Glass - Type II

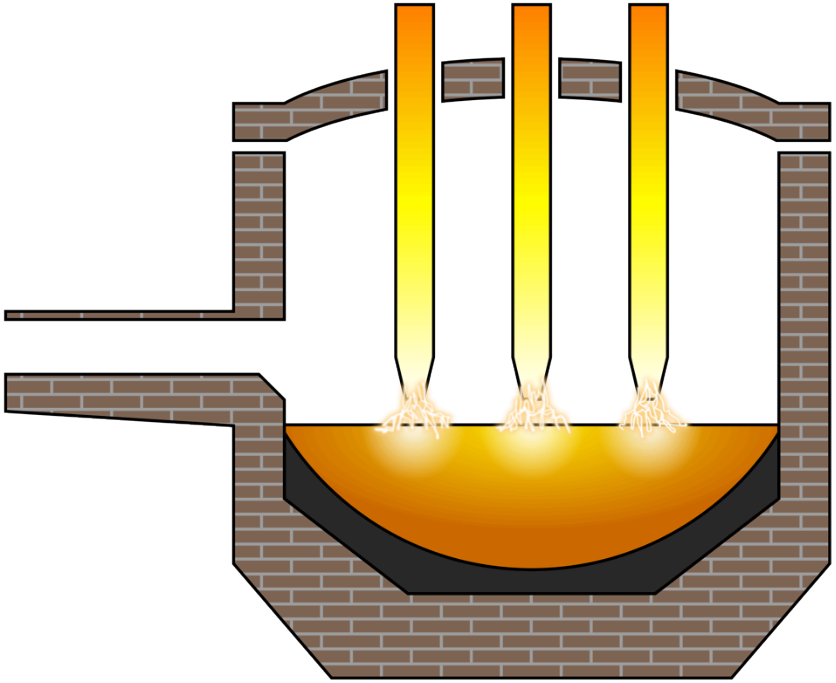
- Also called "fused quartz"
- Produced from quartz crystal powder
- Oxy-hydrogen flame fusion (similar to Verneuille crystal growth)
- "Wet" - 150 to 400 ppm OH from combustion products
- Less metallic impurities than Type I
- Alkali < 5 ppm; Transition metal < 10 ppm; Aluminum 10-50 ppm
- Examples:
  - Homosil & Optosil (Heraeus)
  - OG Vitreosil (TSL)
  - General Electric 104 (G.E.)

Lampworking Considerations

- Because of high viscosity and volatility at high temperatures, lampworking is more challenging than with more common soda-lime-silica and borosilicate glasses.
- Natural gas/oxygen, hydrogen/oxygen and acetylene/oxygen type torches used to reach temperatures of 1700 – 1900 °C.
- Rapid cooling outside the flame necessitates working within the flame at all times.
- Only minor annealing at about 1050 °C is required.
- Cleanliness is essential to avoid surface contaminants leading to devitrification while working the glass.
- Volatilized SiO_2 can redeposit on cooler regions producing a white powdery appearance (bloom). This can be removed by heat or dilute HF acid.

Electric Arc Fusion for Refractories

- Quartz sand is melted in an electric arc furnace at temperatures > 2000 ºC.
- Resulting glass ingots are crushed and ground to size suitable for injection molding or slip casting.
- Shaped articles are dried and sintered (fired) at 1150-1250 ºC.
- Typical products are white, opaque refractory bricks, crucibles, nozzles and pouring tubes used elsewhere in the glass industry. They are called fused silica refractories.
- Not a focus of these lectures.



Heroult-type electric arc furnace. Illustration only. Not intended to represent geometry of actual quartz melting furnace.

Exercise

- From what we have covered today, explain why the amount of water dissolved in silica glass differs between Type I and Type II.
- Which one is greater? Why?
- Would you expect that trend always to be the case? Why or why not?

Next Week

Day Two

1. Synthetic fused silica manufacturing
   Processes and resulting characteristics
   Deliberate addition of modifying chemical species.

2. Modern Applications
   Examples -Telescope mirrors, microlithography optics, optical fiber

3. Summary and Acknowledgements

Acknowledgements

- Most of the illustrations are from manufacturers product brochures, the patent literature or technical literature.

- Useful references include
  - Various editions of *The Encyclopedia of Chemical Technology*
    - » W. Winship; W.H. Dumbaugh and P.C. Schultz; P.S. Danielson; D.R. Sempolinski and P.M. Schermerhorn
  - *Commercial Glasses (Adv. in Ceramics 18)*
    - » P. P. Bihuniak
  - "Fused Quartz Manufacture in Germany," Final Report No. 1202, British Intelligence Objectives Sub-Committee, 1946.
  - See suggested reading list for details.