IMI-NFG Course on Processing in Glass

Spring 2015

(available online www.lehigh.edu/imi)

Lecture 1: Commercial glass compositions, properties and technical considerations – Raw materials

Mathieu Hubert, PhD

CelSian Glass & Solar
Eindhoven, The Netherlands

mathieu.hubert@celsian.nl

Glass is everywhere

- Glass is one of the most ubiquitous materials, it is found everywhere in our everyday lives
- Due to its versatility, glass is found in various applications – a lot of them very “visible”, and also sometimes in more “unexpected” places” – About **100 million tons** of glass are produced every year
- Men have been manufacturing and using glass for more than three millennia, and keep developing more and more applications

Examples of ancient glass articles

Source: http://www.metmuseum.org

Garland bowl, late 1st century b.c

Conical bowl, 2nd–1st century b.c

Glass is everywhere - Examples

Art

www.venicelimousinerent.com

Glass is everywhere - Examples

Bottles – all shapes, sizes and colors…

Glass is everywhere - Examples

At the table

http://mocoloco.com

Glass is everywhere - Examples

In the kitchen

Schott

Eurokera

Source: www.dailymail.co.uk

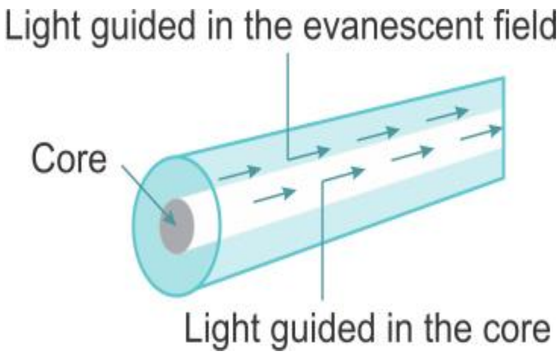
Glass is everywhere - Examples

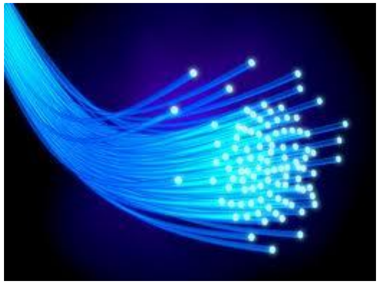
In the lab

Glass is everywhere - Examples

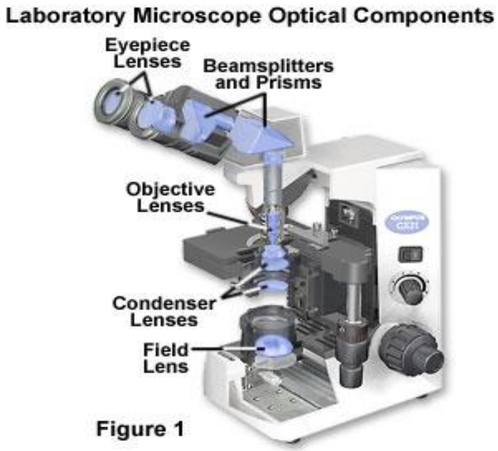
In optics

Optical fibers





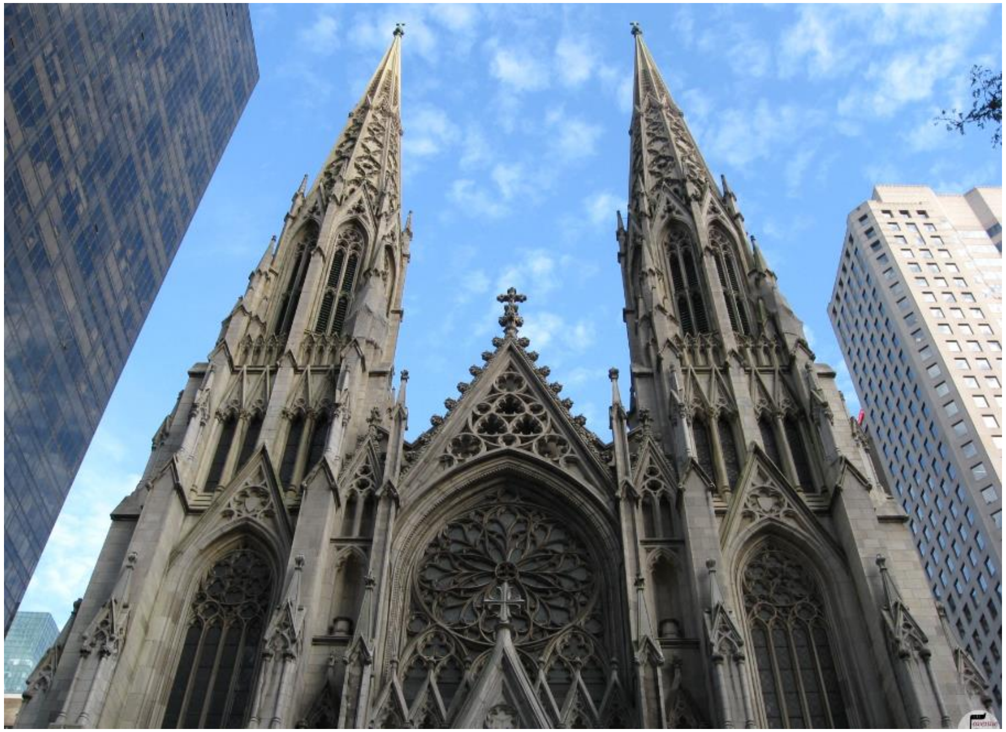
www.ictas.vt.edu



Multiple Mirror Telescope, Arizona

Glass is everywhere - Examples

Buildings – Modern and ancient



Shanghai World Financial Center

Glass is everywhere - Examples

All types of transportation

Glass is everywhere - Examples

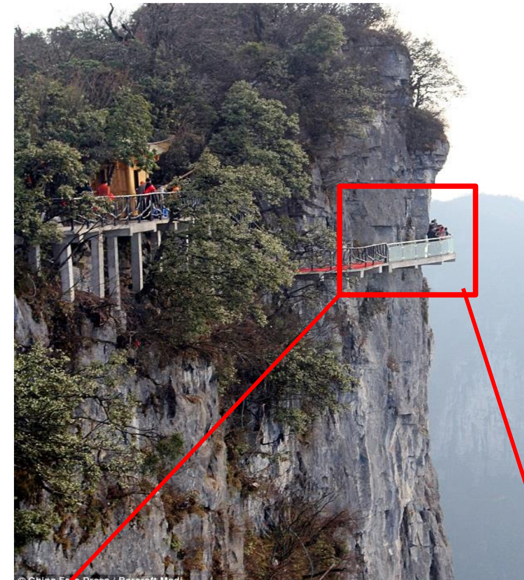
In modern architecture

Apple Store New York

Source: Nypost.com

Observation deck – Willis Tower Chicago

Tianmen mountain, China



Grand Canyon Skywalk

www.tourismontheedge.com

Credit: 360 Chicago

http://i.dailymail.co.uk

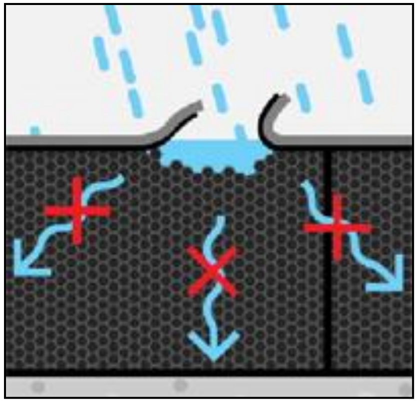
Glass is everywhere - Examples

Buildings - Insulation

Glasswool

Isover – Saint-Gobain

Foamglas®



http://www.actu-environnement.com/

Glass is everywhere - Examples

Solar panels, solar power plants…

http://www.fm.colostate.edu/

P10 Solar power plant, Andalucia, Spanje

Glass is everywhere - Examples

All types of screens

http://www.geekalerts.com

Corning Gorilla® glass

Glass is everywhere - Examples

Reinforcement material

Souce: wikipedia

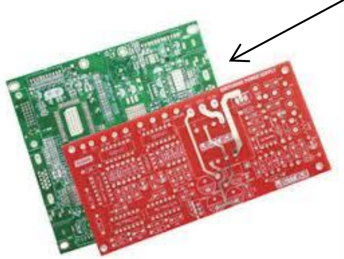
Fiberglass-reinforced materials

www.guizmodo.com

Glass is everywhere - Examples

Reinforcement material






- Ship hulls, surfboards, kayaks...
- Sports cars
- High-end bikes
- Antens, radomes
- Tanks, vessels
- Printed boards
- Wind Turbines
- Helmets and protective equipment
- Orthopedic casts
- ...

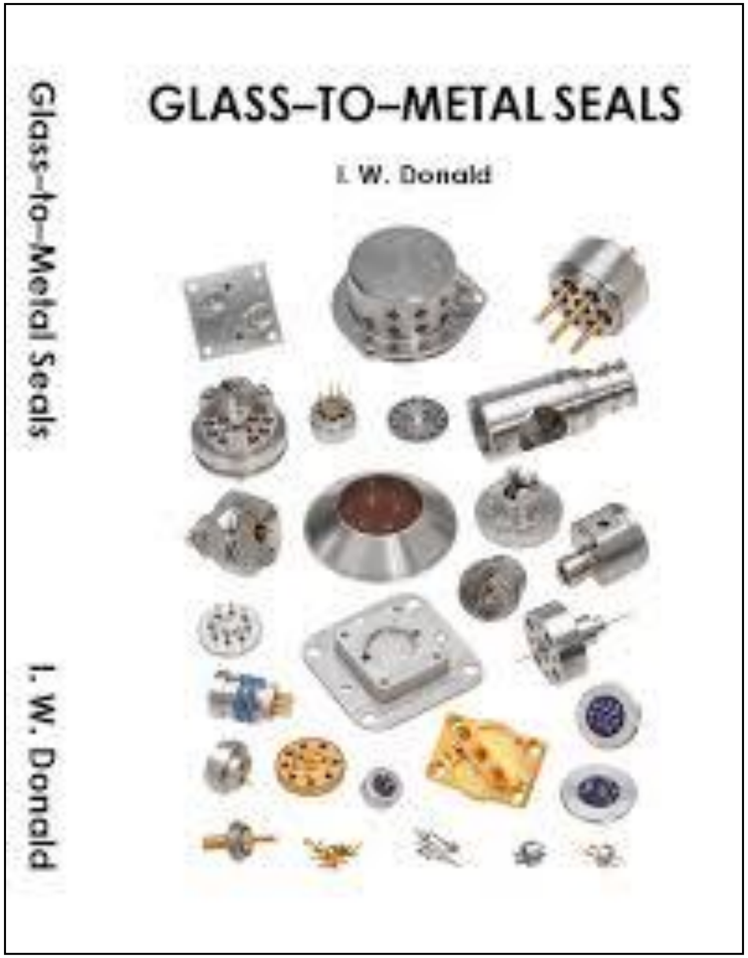




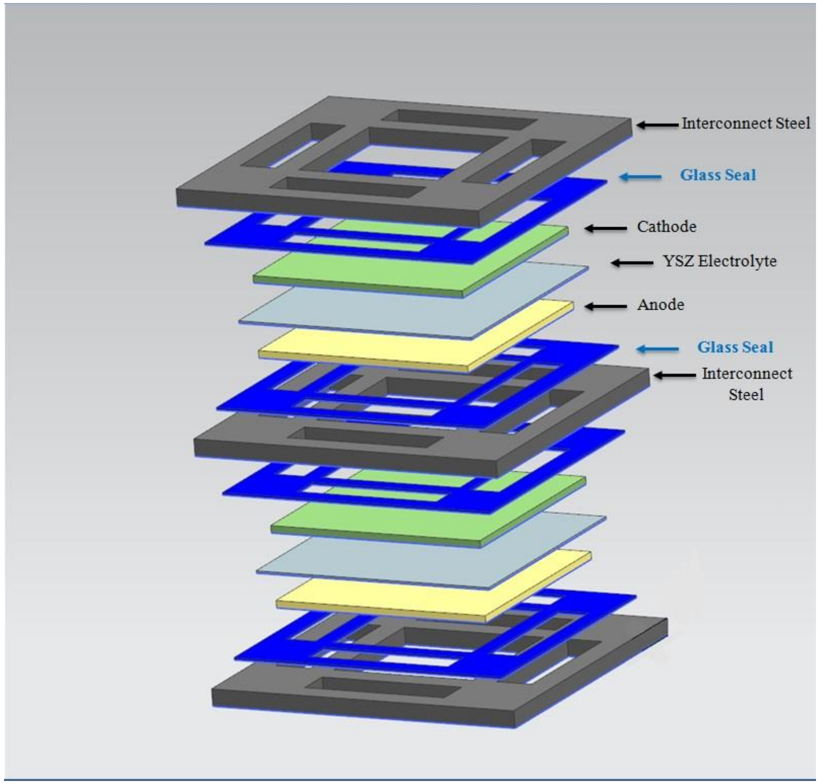
Souce: wikipedia

Glass is everywhere - Examples

Electronics – Glass-to-metal seals



Sealant glass in Solid Oxide Fuel Cells (SOFCs)



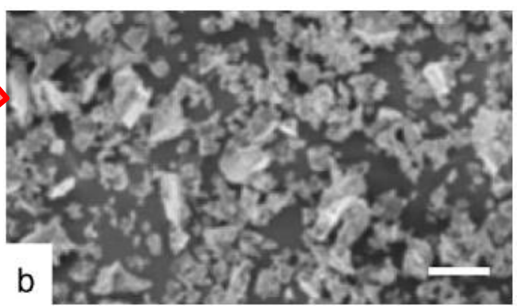
Source: www.mo-sci.com

Glass is everywhere - Examples

Dental applications

Bioactive glass in toothpaste*

Novamin® glass pieces*



*J. Jones, Review of bioactive glass: From Hench to hybrids, Acta Biomaterialia 9 (2013) 4457–4486

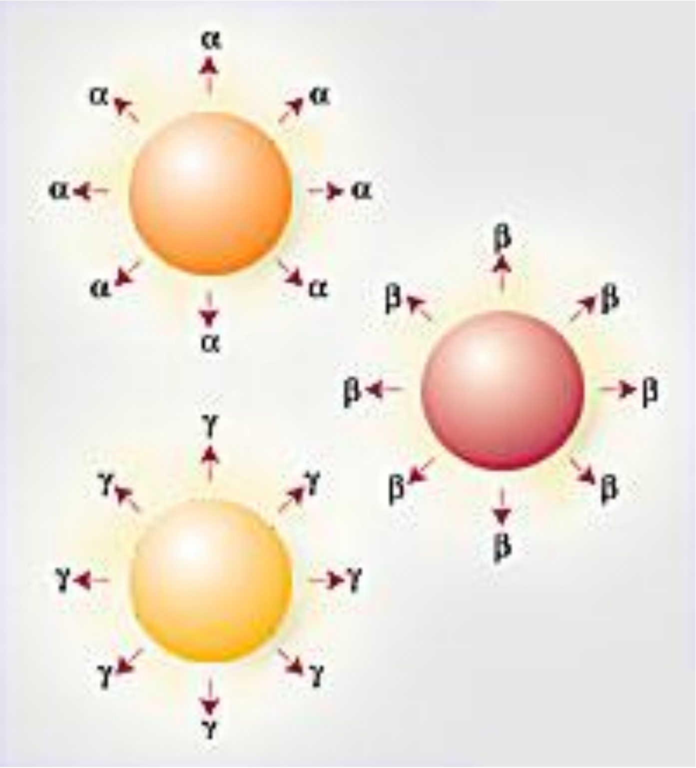
Glass-Ceramics

L. Hench et al., Glass and Medicine, International Journal of Applied Glass Science 1 [1] 104–117 (2010)

Glass is everywhere - Examples

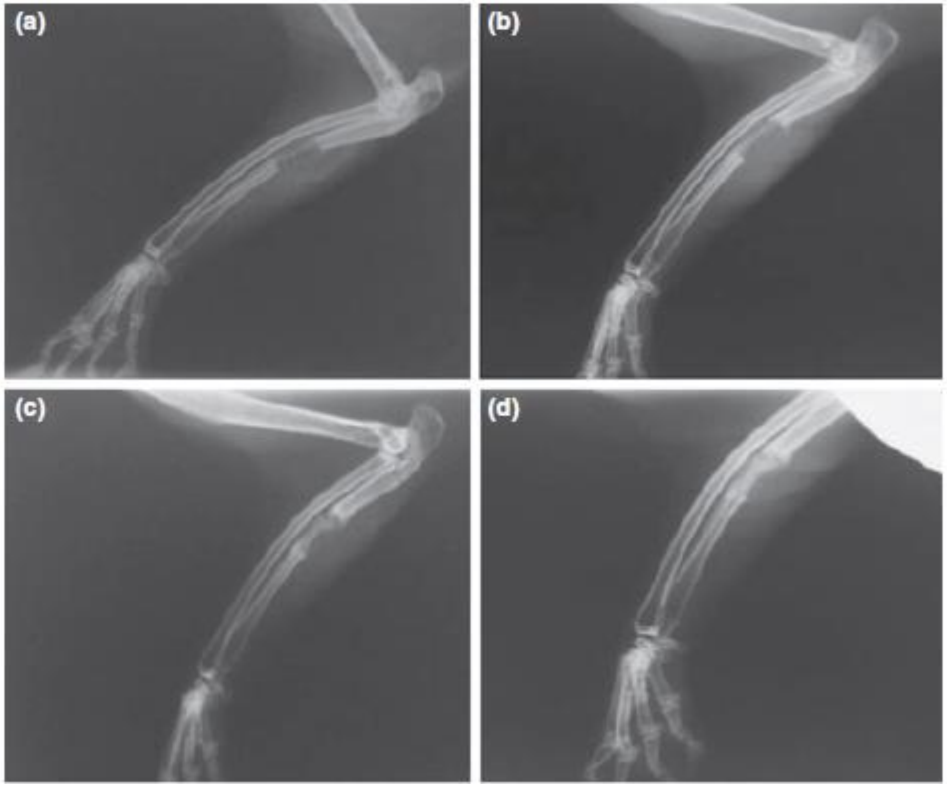
Medical applications

Radioactive microspheres



Source: Mo-Sci Health Care

Scaffold for bone or tissue regeneration



M. Erol-Taygun et al., Nanoscale Bioactive Glasses in Medical Applications, International Journal of Applied Glass Science 4 [2] 136–148 (2013)

Glass is everywhere - Examples

But also…

Glass beads for water purification

SiLibeads®

Bioactive glasses in cosmetic products

Source: Schott

Glass for night-vision enhancement (chalcogenide infrared-transparent glasses)

Source: photonics.com

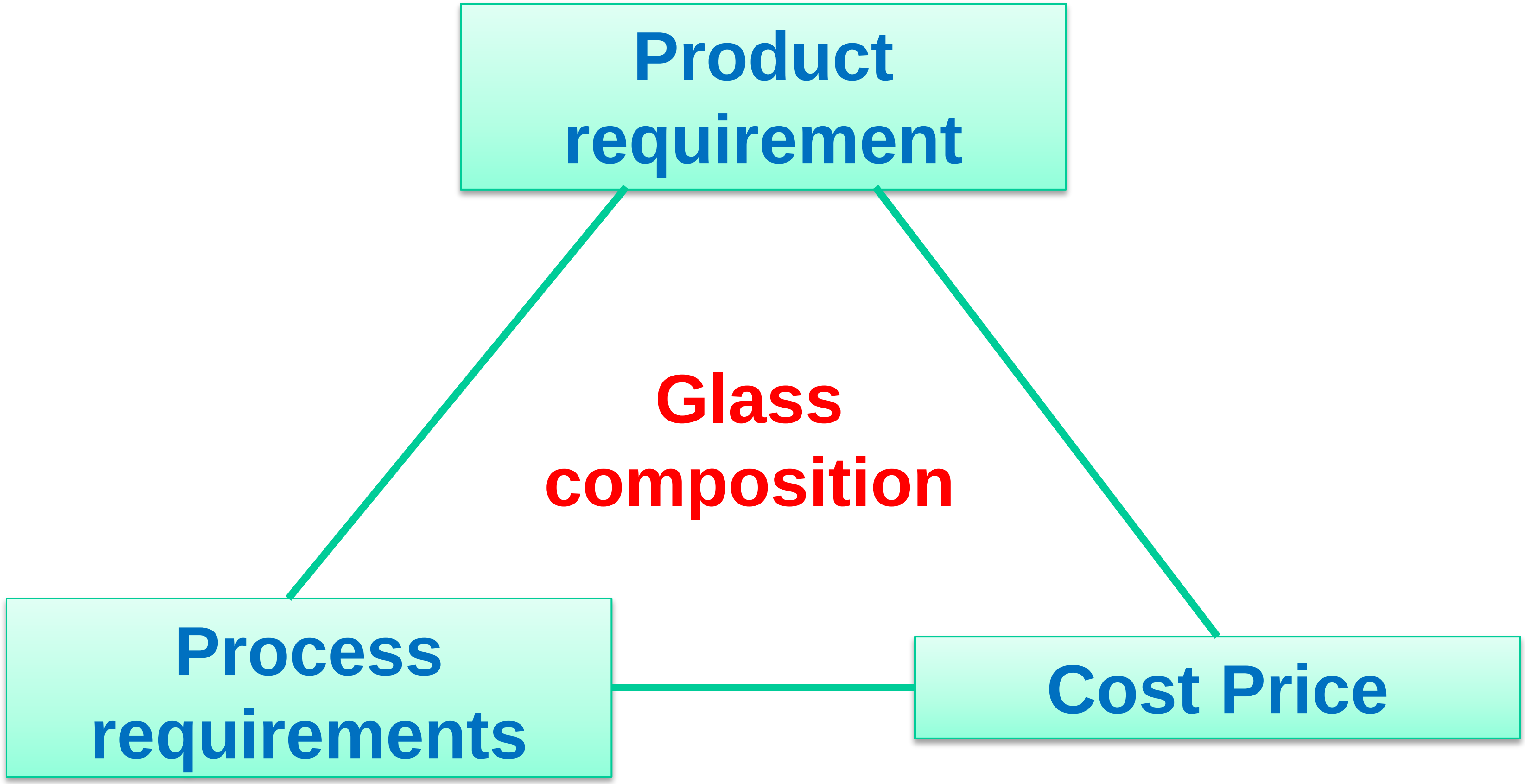
Glass is everywhere - Examples

And many more…

More examples of where glass is used and on the future of glass can be found for instance:

- IMI-NFG technical library
- Corning videos “A day made of glass”
- ICG Roadmaps of glass R&D “Making glass better” (K. Bange, A. Duran, J. Parker – 2nd edition 2014)
- Diverse scientific journals on glass (JACerS, IJAGS, JNCS…)
- ….

How do I choose my glass composition?



Outline of this lecture

- **Main commercial glasses** *(brief – non exhaustive survey)*
  - Compositions
  - Properties / Uses
  - Technical considerations for industrial melting

- **Raw materials and batches** *(industrial)*
  - Types of raw materials / sources
  - Raw material selection
  - Batch preparation

Main types of commercial glasses – 1/2

Main Group	Application	Characteristics
Soda-Lime-Silica glass *($Na_2O·CaO·SiO_2$)*	- Flat glass - Container glass - Tableware - Lamp glass (lighting) - Lenses	- Mass production - Low cost
Sodium-borosilicate *($Na_2O·B_2O_3·SiO_2$)*	- Laboratory glass (ex: Pyrex® or Duran®) - Cooking utensils - Headlights	- Thermal shock resistant
E-glass *($CaO·Al_2O_3·B_2O_3·SiO_2$)* *Sometimes without B_2O_3 other components: MgO, TiO_2	- Textile glass fiber - Reinforcement fibers for plastics - Fibers for printed circuit boards	- Mechanical strength - Low electrical conductivity - Fiberizability
A-glass *($Na_2O·CaO·B_2O_3·SiO_2$)*	- Glass wool (insulation) - Glass fiber (reinforcement)	- Fiberizability - Low cost

Main types of commercial glasses – 2/2

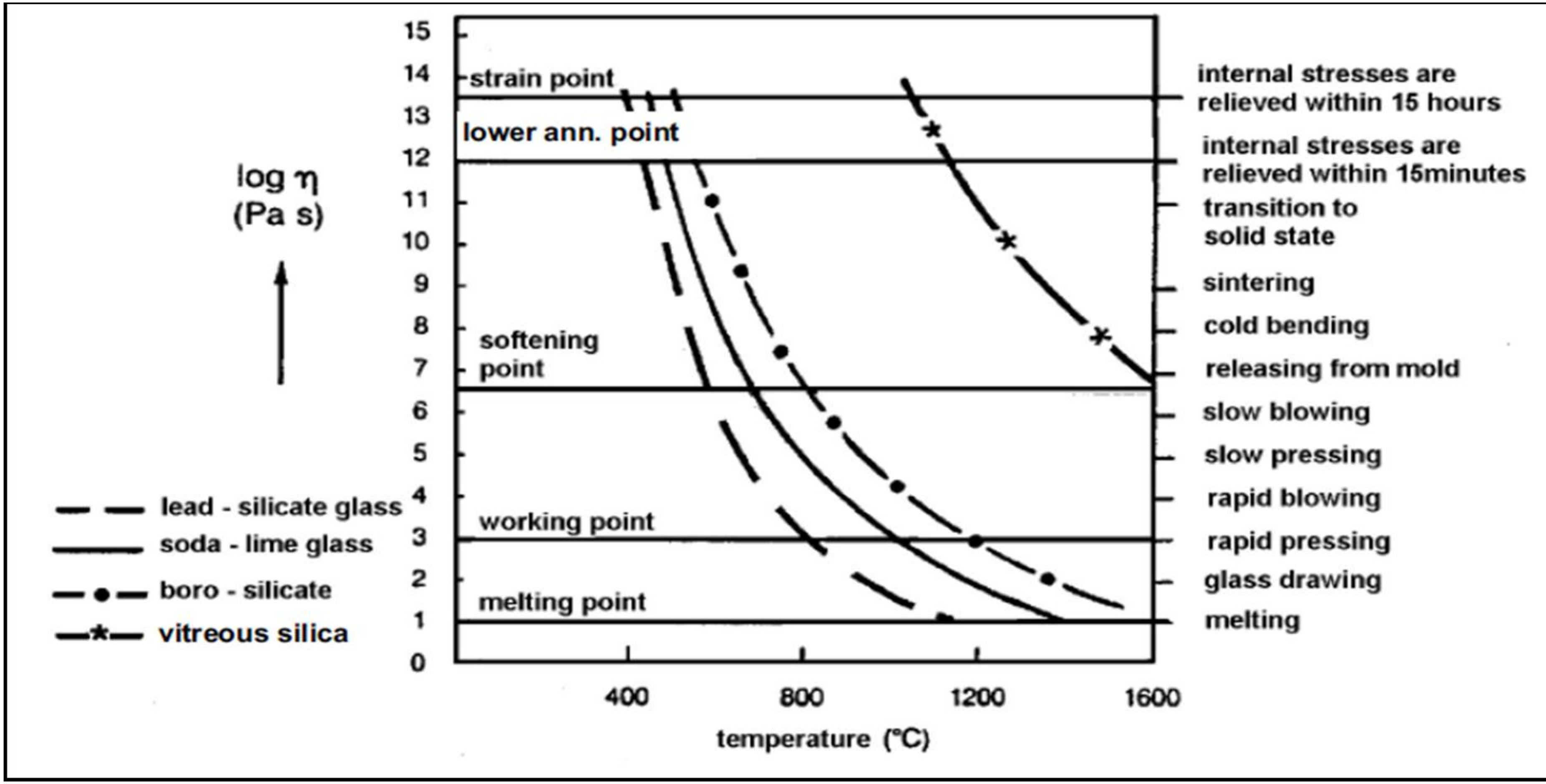
Main Group	Application	Characteristics
Display glass* *($Al_2O_3 \cdot CaO \cdot B_2O_3 \cdot BaO \cdot SiO_2$)*	- Substrate glass for displays (TFT-LCD)	- Low electrical conductivity - Ultra thin (down to 50 µm) - High melting temperatures
Lead crystal *($PbO \cdot K_2O \cdot SiO_2$)*	- Art glass - Tableware - Decoration enamels	- High purity - High refractive index value
Vitreous silica *(SiO_2)*	- Optical glass fiber (telecommunication) - Halogen lighting - Laboratory and chemical equipment	- Purity - High-temperature resistance - Very high thermal shock resistance

* Several types of display glasses exist, depending on their use (e.g. in contact with electronics or cover glass). Cover glasses also contain alkalis (mainly sodium) to enable strengthening by ion exchange treatment

Example of some of the glass properties

	Unit	Soda-lime-silica	Boro-silicate	E-glass	A-glass	Quartz glass	LCD glass
ρ density	kg/m^3	2500	2230	2530	2460	2200	2500
α: thermal expansion coefficient	K^{-1}	92×10^{-7}	33×10^{-7}	50×10^{-7}	90×10^{-7}	5×10^{-7}	35×10^{-7}
λ: heat conductivity at 100 °C	W/(m·K)	1,1	1,3			1,48	1
C_p : specific heat at 100 °C	kJ/(kg·K)	0,87	0,85			0,84	0.7
E: Young's modulus	Pa	72×10^9	64×10^9	77×10^9	74×10^9	74×10^9	70×10^9
Glass process tem-peratures	°C						
- working point :	$\log \eta = 3$	990	1250	1070		2400	
- softening point:	$\log\eta = 6,6$	700	820	840		1670	
- annealing point:	$\log \eta = 12,4$ η in Pas	520-540	565	670		1190	710
*n_d : refractive index		1,52	1,47	1,55	1,54	1,46	1.51

Example: viscosity of commercial glasses



Important note: melting at higher temperatures induce higher costs for melting (energy required) and can also require use of materials with higher thermal resistance for the melting (e.g. refractories), i.e. more expensive

Commercial glasses compositions

- As seen from the first tables, **different types of applications require different types of glass**

- The composition of the glass is governed by the targeted properties/application, as well as technical and economical considerations

- **Each element brings specific benefits** (but also constraints), and the final commercial composition corresponds to the **best compromise** between these different aspects

- Only the main elements have been presented (SiO_2, Na_2O, CaO, MgO, B_2O_3, Al_2O_3…), but commercial glass batches (often) include numerous other elements in lower quantities to bring specific features (to modify the batch and/or the final glass properties)

Commercial glasses compositions

- These elements added in smaller quantities can include:
  - ✓ Coloring agents
  - ✓ Fining agents (to promote homogenization during industrial melting and removal of bubbles)
  - ✓ Melting flux (to promote melting at lower temperatures)
  - ✓ Redox active species (to oxidize or reduce the glass melt)
  - ✓ *Nucleating agents (for production of glass-ceramics)*
  - ✓ Other elements to improve specific properties (e.g. modify the refractive index)

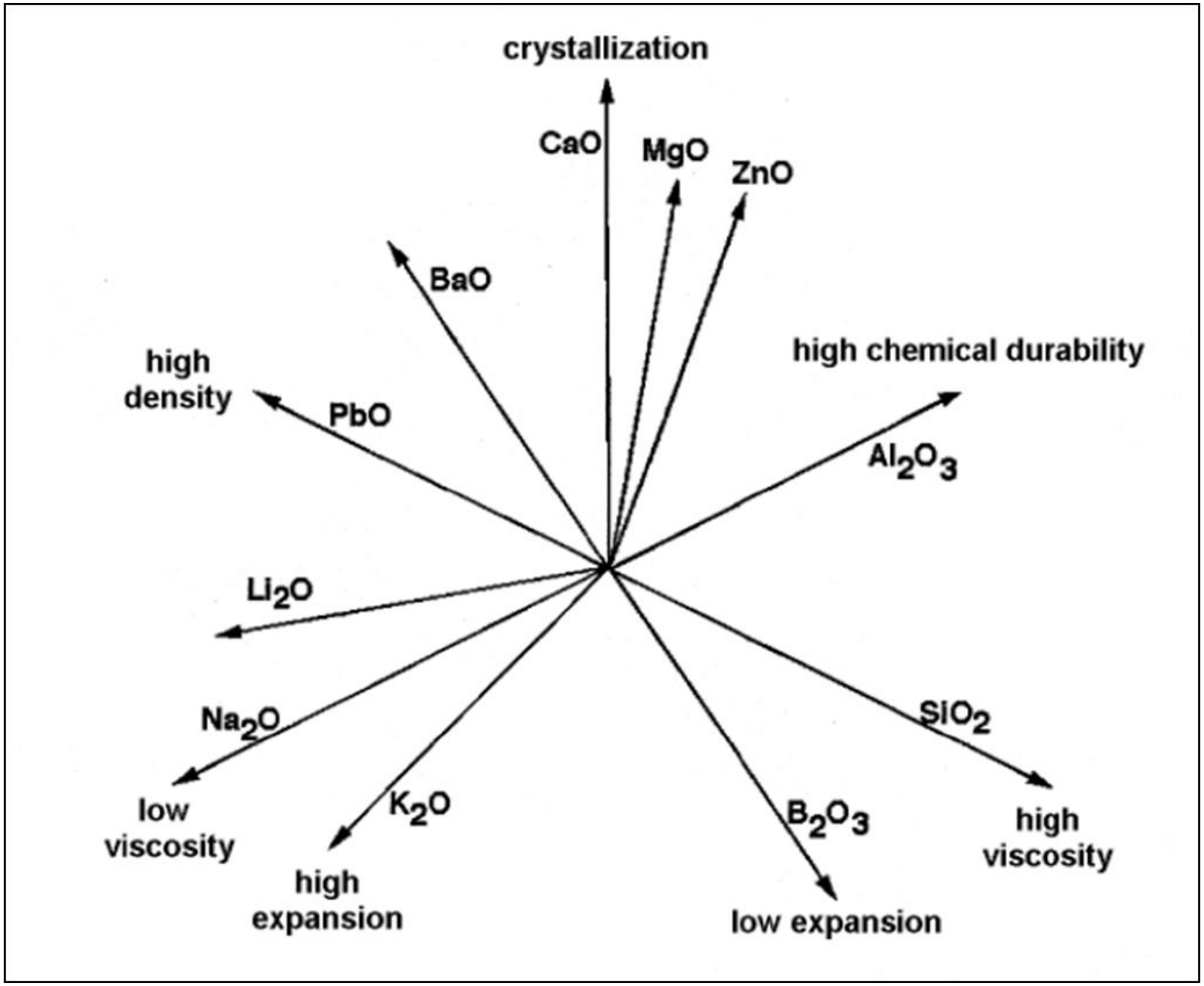
- The final combination of all these elements will govern the behavior of the batch during melting and the final properties of the glass produced

From the glass composition to the raw materials

- Each element (besides impurity) is added to the glass batch to provide some specific property regarding the glass itself and/or for influencing the melting/processing of the glass
- So far, the glass compositions have been expressed in “% oxide”, but the raw materials are not necessarily introduced in this form
- Each element can be **classified as function of its role** in the final glass and/or in the melting process (network forming, network modifying, intermediate oxides, fining and fluxing agents, coloring ions, cullet…)
- The choice of the raw material will be based on several criteria, described in the following slides

Composition in mass%	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	Diverse
Container glass								
- Flint	72,6	13,7	0,5	11,0	0,1	1,6	< 0,05	0,2 SO_3; 0,1 TiO_2
- Green	72,0	15,1	--	8,4	2,1	1,1	0,4	0,02-0,06 SO_3 0,25 Cr_2O_3
- Amber	72,7	13,8	1,0	10,0	--	1,9	0,2	0,05-0,08 SO_3
Clear Float glass	71	14	0,8	9	5	1-1,5	0.080	0,2-0,3 SO_3
Tinted Float glass	70	14	0.8	9	5	1-1,5	0.3-1.5	0,2-0, 3 SO_3
Display **- LCD- glass**	58- 60	<0.1	<0.1	5 - 7	0 - 1	15		±10 B_2O_3 ± 10% BaO+SrO
Lighting glass	72,4	17,4	--	5,3	3,7	0,8	--	
Tableware	75,6	13,5	4,1	3,7	2,6	0,4	0,02	
E-Glass*	55,2	0,5	0,5	17,7	4,3	14,8	0,3	0-10 B_2O_3
Insulation wool	64	15.5	1,2	7	3	3.5	0.25	4,5 B_2O_3 ; 0,15 SO_3
Borosilicate (Pyrex)	80,2	4,5	0,3	0,1	--	2,6	0,07	12,3 B_2O_3
Opal glass	66,9	13,3	2,2	4,8	0,4	6,9	0,08	Up to 6 Fluoride 1,6 BaO
Crystal glass	58,5	1,3	13,1	--	--	--	0,02	25,2 PbO
Lead crystal	54,9	0,2	12,3	--	--	--	0,02	32,0 PbO
Roman glass (first century AD)	70,0	16,5	1,0	7,0	0,6	5,0	--	--

Schematic – element vs. effect on properties



Main elements and raw materials employed

- **Network forming oxides**
  - SiO_2, B_2O_3, P_2O_5, GeO_2
  - *Non-oxide components: fluorides, halides, chalcogenides (As_2S_3, GeS_2)*
- **Network modifying oxides**
  - Na_2O, K_2O, Li_2O
  - CaO, BaO, MgO, SrO
- **Intermediate oxides**
  - Al_2O_3, PbO, ZnO, ZrO_2
- **Fining agents/redox active components**
  - Sulphates: Na_2SO_4, $CaSO_4$
  - Oxides: As_2O_3, Sb_2O_3, CeO_2
  - Chlorides: NaCl - Nitrates: KNO_3, $NaNO_3$ - Carbon
- **Fluxing agents**
  - CaF_2, Spodumene (lithium raw material), blast furnace slags/calumite
- **Colouring agents**
  - Fe_2O_3, Cr_2O_3, CoO, Mn_2O_3, Se, Fe^{3+}/S^{2-}, rare earth oxides, sulfides, selenides
- **Cullet (recycled glass, own or external cullet)**

Raw Materials

Raw materials choice – What is to be considered?

- **Chemical composition**
  - Stability
  - Hygroscopicity (clogging of hygroscopic compounds)
  - Impurities
    - Coloring oxides (e.g. iron oxides, chromium oxides,…)
    - Heavy mineral (zircon, zirconia, chromite,…), CSPs
    - Organic material → effect on redox & foaming
    - Fluorides, chlorides, sulfur (in synthetic soda, cullet, clays, dolomite, slags, filter dust): → emissions

- **Melting Characteristics**
  - Melting-in
  - Melting enthalpy
  - Mass losses
  - Grain sizes
  - Easy to melt forms: clay, feldspars for Al_2O_3 in glass

- **Costs** (often determined by raw material production technology)

Sources of raw materials

- The raw materials employed may be either **mineral** (obtained from extraction from the soil / mining…) or **chemical** (obtained by chemical processes)

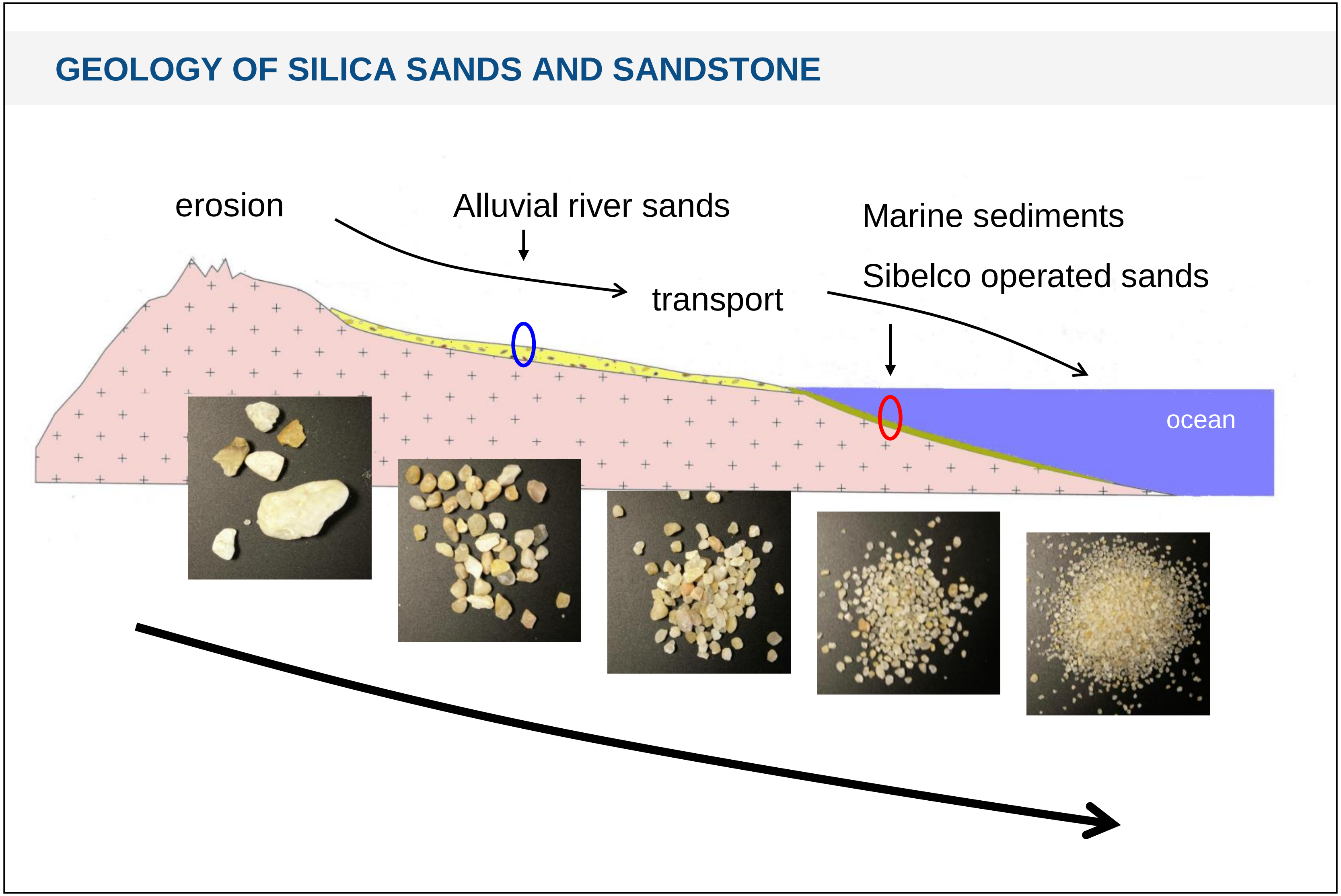
- The source of the raw material has to be considered. The main considerations to take into account are listed below:

Mineral ingredient	**Chemical ingredient**
• Less expensive • Often contaminated • Variable composition • Limited process control • Multiple sampling required • *Delivery under certificated is often difficult*	• More expensive • Higher purity • (almost) constant composition • Process control available • Singular sampling often sufficient • *Delivery under certificate possible*

Network forming elements – SiO_2

- Silica SiO_2 is the main “constituent” in all the commercial glasses mentioned so far
- SiO_2 is available from natural sources as **quartz sand** (silica), sandstone & quartzite. Only silica is sufficiently pure for most glass productions. It occurs in primary and in secondary quartz deposits
- Secondary silica sand deposits are found in abundance all over the world. They comprise of silica sand carried along by wind and water. During this transport it has been classified on grain size.
- The purity may vary widely
- **It is important** from an economic perspective that the properties of the raw sand, still unprocessed, are not too far from the desired glass grade parameters

Scheme of erosion of silica rock and transport plus deposition of silica sand erosion product (source: Sibelco)



Network forming elements – SiO_2

- The **grain size** and **mineralogical parameters/compositions/low level impurities of glass sands** are stringent, it is rare for a glass sand deposit to satisfy these parameters without some processing.
- The preferred grain size distribution of glass sand is predominantly between 0.125 mm and 0.500 mm. High % of finer or coarser material in the sand may result in unacceptable processing losses.
- The location and percentage of **iron** in the sand is important (for the effectiveness of the sand refining process in reducing or removing it)
- Humic or organic acids in the depositional environment often play an important role in dissolving and removing iron from the sand
- The content of **heavy or non-meltable refractory minerals** (hardly soluble in silicate melt) is also an important factor

Network forming elements – SiO_2

Processing techniques for silica sand comprise

- size reduction (sieving, hydro-sizer)
- washing
- sieving
- classification
- attrition (abrasion) scrubbing
- magnetic separation
- density/gravimetric separation (spirals)
- flotation
- thermal drying and milling

Network forming elements – SiO_2

- Other sources of silica comprise:
  - **Cullet** (recycled glass)
  - **China clay or Kaolin** *(Al_2O_3-$2SiO_2$-$2H_2O$)*
  - **Feldspar / Nepheline** components *(R_2O-Al_2O_3-$xSiO_2$)*

- In E-glass (continuous filament glass fiber) production, kaolin (china clay) is used to provide alumina to the glass composition.
- For zirconium oxide containing glasses, the raw material, **zirconium silicate** (zircon: $ZrSiO_4$) can be used.
- In general individual sand & alumina particles will dissolve less rapidly into the melt than fine china clay particles, introducing SiO_2 through clay is beneficial compared to the use of pure silica sand plus alumina.

Network forming elements – B_2O_3

- B_2O_3 containing glasses are often used for applications that need a high resistance against thermal shocks (ex: Pyrex®). Borosilicate glasses often show a low thermal expansion coefficient.

- If the alkali content in the glass should be kept at a low level, the boron containing raw material to be used is **boric acid** (H_3BO_3) or **colemanite** ($Ca_2B_6O_{11}$-$5H_2O$), like in the case of E-glass

- In **LCD glasses, alkali oxides cannot be accepted** and boric acid is often used in the batch composition to supply the boron oxides

- Sodium-tetraborate, better known as **borax** ($Na_2B_4O_7$-$10H_2O$), is used for sodium-borosilicate glasses, for instance for insulation glass wool.

- **Boron oxide** (B_2O_3) is also employed in some high-end productions

Network modifying elements

- **Alkaline and alkaline earth oxides** are added to the glass in order to **increase the melting rate**, to **decrease the viscosity** of the molten glass and to obtain a good processing performance during forming. The alkali oxides are effective in improving the fusibility (“fluxing agent”)

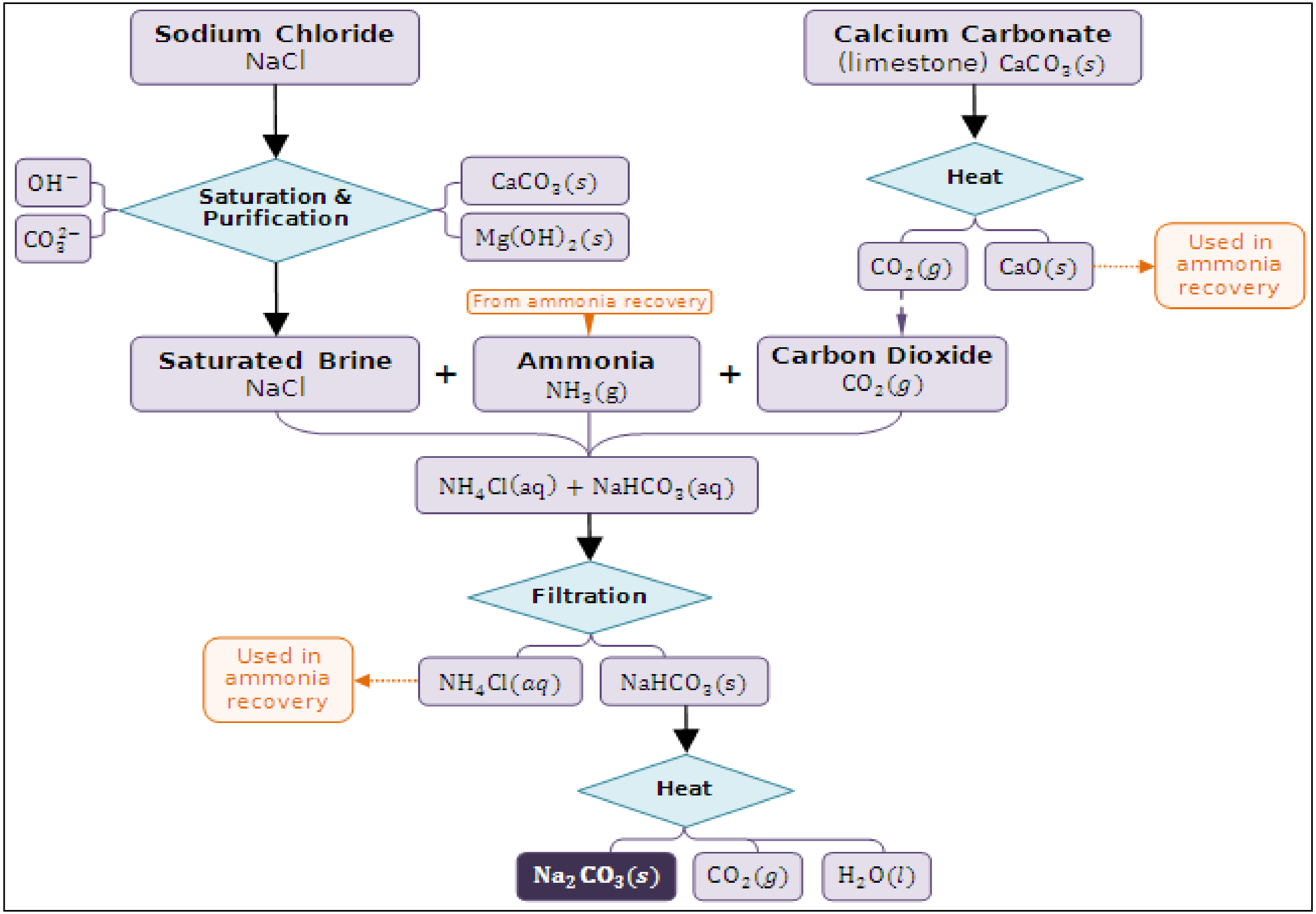
- Alkali carbonates react with earth alkali oxides (or earth alkali carbonates) or with silica sand far below the SiO_2 melting point. Alkali silicates or alkali-earth alkali silicates are formed during batch melting.

- However, the **chemical durability of the glass decreases by the alkali oxides**. Replacing part of the alkali oxides by earth alkali oxides will increase chemical durability.

Alkaline elements – Na_2O

- Na_2O is mainly introduced in the form of **soda ash** (Na_2CO_3), produced by the Solvay process (flow chart on the next slide)
- Due to this process, the soda will contain some residual NaCl as impurity (0.09-0.3 wt%)
- Soda from natural sources (natural trona soda) is also used in industrial glass production (contains about 0.05 wt% NaCl)
- Soda may absorb large quantities of water (below 35.4°C the compounds Na_2CO_3-$7H_2O$ and Na_2CO_3-$10H_2O$ are formed). This has to be considered when preparing and transporting the batch
- Other Na_2O-carriers are sodium **feldspars, nepheline syenite, borax, sodium sulfate** (generally used as fining agent), soda-lime-silica glass **cullet**

Flowchart of the Solvay Process



http://www.boredofstudies.org/wiki/images/1/1d/Sci_chem_industrial_solvay_flowchart.png

Alkaline elements – K_2O

- In manufacturing lead crystal glass, potassium oxide K_2O (increasing the refractive index of the glass products) instead of Na_2O is added especially via **potassium carbonate** K_2CO_3.
- As soda ash, K_2CO_3 is prepared from chlorides (potassium chloride)
- K_2CO_3 is very hygroscopic (should be kept in dry, isolated storage)
- Other K_2O-carrier include **potassium feldspars** ($K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$) (K and Al containing mineral, notably found in Western Europe)
- Potassium is sometimes introduced as **potassium nitrate** (KNO_3) which can also serve as an oxidizing agent in potassium containing glass melts.

Alkaline elements – Li_2O

- Sometimes lithium oxide is added in small concentrations as a fluxing agent. The most important lithium oxide containing raw material is **spodumene** ($Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$) or **synthetic lithium carbonate** (Li_2CO_3)

- Lithium oxide is expected to improve the melting rate as a fluxing agent. Small additions of lithium oxide can have a strong influence on some glass properties like the expansion coefficient and the viscosity.

- Li_2O in the molten glass may increase the attack on the melting tank refractory materials.

Alkaline-earth elements – CaO

- **Limestone (**$CaCO_3$) is by far the most important mineral used for supplying CaO.
- For the manufacturing of E-glass, **colemanite** ($Ca_2B_6O_{11}.5H_2O$) is used as a CaO-carrier apart from also supplying boric oxide.
- **Dolomite** ($MgCO_3 \cdot CaCO_3$) will be used when besides CaO also MgO is desired in the glass composition
- **Quick lime** (CaO) or hydrated lime ($Ca(OH)_2$) are sometimes used in glass manufacturing (energy saving during melting as no decarbonation needed). However, their production from limestone are energy intensive processes (raw material more expensive)
- **Lime rich filter dust** are produced by scrubbers and filters applied to control emissions from glass furnaces

Alkaline-earth elements – MgO

- The main MgO carrying raw material is **dolomite** ($MgCO_3 \cdot CaCO_3$). Dolomite often contains chlorides and fluorides as impurities.

- Dolomite is prone to decrepitation (*during heating of dolomite grains, decomposition will take place above a certain temperature, releasing CO_2 gas. Within the dolomite grains, this evolved CO_2 gas builds up a pressure and the grain can burst by this pressure)*

- Other MgO containing raw materials are **magnesium carbonate** ($MgCO_3$), as a mineral often contaminated with Fe_2O_3, or reasonably pure $MgCO_3$ generated as a waste product in the alkali industry. Often being used is the **synthetic basic magnesium carbonate** ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$).

Intermediate oxides – Al_2O_3

- The **intermediate oxides give the glass more stability**. They **decrease the tendency to crystallize**, **increase the chemical resistance** and with Al_2O_3 a favourable influence on the tensile strength has been observed.

- Aluminum oxide also called **alumina or corundum** (Al_2O_3) is by far the most frequently used intermediate in the glass compositions

- Pure alumina powder / grains dissolve very slowly in the glass melt

- Often Al_2O_3 is added by raw materials such as **kaolin, feldspar or nepheline syenite**. Nowadays also the much more expensive synthetic ingredient aluminum oxide is being used

- Aluminum oxide occurs also in **blast furnace slags** (10 - 15 mass%) and as an impurity in sand and dolomite (0 - 0.3 mass%)

Fining agents

- Fining agents are additives to enhance the removal of dissolved gases and gas bubbles (e.g. seeds of typically 0.05 – 0.5 mm diameter) from the melt in order to get seed-free glass (Lecture 2).

- In the industrial manufacture of glass, so called fining agents are added to a maximum of ± 1.0 wt %.

- The most widely used fining agent is **sodium sulfate** (Na_2SO_4) (salt cake) especially used for soda lime silica glass, E-glass (sometimes in combination with reducing agents such as carbon or oxidizing agents such as nitrates, to modify the fining onset temperature)

Fining agents

- Besides **sodium sulfate** (Na_2SO_4), other fining agents commonly found in the glass industry include:

  - ✓ Antimonate or Arsenate (Sb_2O_5, As_2O_5)
  - ✓ Sodium chloride (NaCl)
  - ✓ Cerium oxide (CeO_2)
  - ✓ Tin oxide (SnO)
  - ✓ Calcium sulfate ($CaSO_4$)

- The choice of the fining agent (and potential combination with oxidizing or reducing agents) will be based on the desired temperature range for the fining, possible restrictions on the composition, and technical considerations

Fluxing agents

- **Fluxing agents are additives for accelerating the batch melting reactions**. The action of these compounds may rely on several principles:
  - ✓ Lowering the temperature at which the first aggressive melt phase occurs
  - ✓ Decreasing the surface tension of the batch melts, which improves wetting of the sand particles by these reactive melts
  - ✓ Formation of low viscous eutectic melt phases
  - ✓ Some materials in the batch need less reaction enthalpy upon melting compared to the raw materials that are replaced (e.g. cullet replacing normal batch)
  - ✓ Some raw material enhance the heat transfer into the batch blanket

Fluxing agents

- The main types of fluxing agents found in the glass industry include:

  - ✓ Fluorspar (CaF_2)
  - ✓ Lithium carbonate (Li_2CO_3)
  - ✓ Spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$)
  - ✓ Sodium sulfate (Na_2SO_4)
  - ✓ Potassium / Sodium Nitrates (KNO_3 / $NaNO_3$)
  - ✓ Blast furnace slag (e.g. Calumite®)
  - ✓ Cullet

Table 1.1
Chemical Composition (%)

SiO_2	36.50%
Al_2O_3	9.00%
Fe_2O_3	0.28%
TiO_2	0.50%
CaO	40.00%
MgO	11.00%
Total S	0.90%

http://calumiteint.com/

Cullet – Recycled glass

- The waste glass is reworked into **cullet** (cullet size ranging from a few mm up to 2 cm) purified (removal of metal, ceramics, organic components) and supplied to the furnace together with the original batch.
- **Today, cullet has become the main raw material in various glass productions (up to 90 wt% in the batch for some types of glass)**
- **Own (internal or in-house) cullet**: Cullet originating as waste from within the own production process.
- **Foreign (external) cullet**: Cullet from other glass plants and recycled glass cullet (domestic waste) from the glass collection banks. Industrial foreign cullet may originate from post-processing activities of glass (cutting or flat glass or fabrication of automotive glass or windows) or from replacing returnable bottles by new bottles

Cullet – Recycled glass

- **Advantages of cullet**

  ✓ **lower melting energy** than the raw materials (it has been melted previously and there is no endothermic decomposition of carbonates when melting cullet).

  ✓ Cullet can act as a **fluxing agent** and it decreases the melting energy. The **energy savings when 100 % cullet is used is about 25-30 %** compared to supplying 100 % regular batch.

http://precisionrecycling.com/

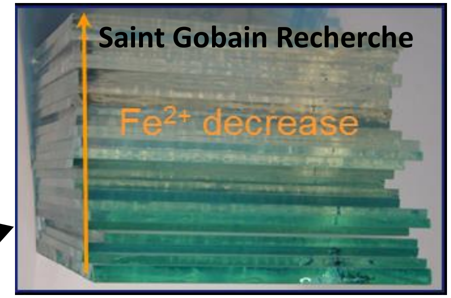
Cullet – Recycled glass

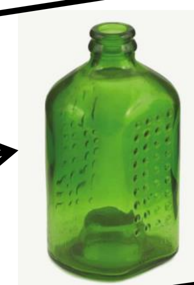
- **<u>Disadvantages of cullet</u>**

  - ✓ When using own cullet, there are no specific disadvantages, provided the cullet is stored clean and dry and the cullet pieces are not too fine.
  - ✓ Very fine cullet may lead to **extra foaming** and glass **dust carry-over**.
  - ✓ Application of foreign (external) cullet may bring some risks
    - ✓ The composition of the cullet may vary.
    - ✓ Impurities of concern (to be removed)
    - ✓ Ceramics, Stones, China (Porcelain)
    - ✓ Metals: Ferro and nonon-Ferro (Al, Ni, Cu, Pb,…)
    - ✓ Glass Ceramics
    - ✓ Colored glass from flint cullet
    - ✓ Organic components de-stabilizing redox state & color of to be produced glass

Coloring elements – transition metals

Ion	Content expressed as	Color effect
Fe^{2+}	Fe_2O_3	green
Fe^{3+}	Fe_2O_3	soft yellow
Co^{2+}	Co_3O_4	blue
Ni^{2+}	NiO	brown
Cr^{3+}	Cr_2O_3	green
Cr^{6+}	Cr_2O_3	soft yellow
Mn^{3+}	MnO_2	purple
Cu^{2+}	CuO	blue green





Reminder: Fe is always present as an impurity from the raw materials. The iron content must be carefully controlled as it has a strong impact n the final coloration of the glass

Coloring elements – other elements

- Residual **ferric iron (Fe^{3+}),** in combination with **sulfides** (reduced molten glass) and alkali components, will cause formation of amber chromophore, coloring the glass **amber**.
- **Cadmium sulfides** (CdS) for **yellow** glass
- **Cadmium selenides** (CdSe) or **Gold chloride** $AuCl_3$ with reduction agent (forms very small gold particles in the glass) for **red** colorizing
- **Selenium** is the colorizing agent for **bronze** glass
- **Cerium oxides**, to oxidize the melt and for absorption of X-Rays. At high concentrations cerium oxide may colour the glass **light yellow**
- A mixture of **Nd_2O_3 & Pr_2O_3** colorize the glass **blue**
- NB: A combination of selenium + cobalt can be used as "decolorizing" agent in flint glass production to mask the coloration due to the presence of iron as impurity

Example cost price of raw materials

Typical price levels (2009) for raw materials applied in the glass industry, in EU **excluding transport costs**.

Mineral ingredients		Synthetic ingredients/ Treated Cullet	
	Euro/metric ton		Euro/metric ton
Quartz sand (regular)	10-20	Na-carbonate (soda ash)	200-250
Quartz sand white	30-40	Na-sulfate	100-150
Quartz sand (milled)**	80 – 100	Na-nitrate (incl. transport)	500-600
Dolomite (1)	25-35	Borax (pentahydrate)	300-400
Dolomite (2) low iron	50-60	K-carbonate	800-1000
Feldspar	100-130	Boric acid	550-650
Nepheline Syenite	100-130	Portachrom	300-450
Limestone	20-40	Cokes	300-400
Calumite	30-45	Mixed Cullet*	55-60
Colemanite	300-350	Flint cullet*	60-75
(incl. transport)	400-450	Green cullet*	60-65
		Flat glass cullet*	70-80

Example of mineral raw materials composition

Raw material	Chemical Composition (mass %)	Tolerance (mass %)	Grain size distribution (example)
Quartz sand (for flint glass)	SiO_2 > 99.0 Fe_2O_3 < 0.030 Cr_2O_3 < 0.0002 Al_2O_3 < 0.3	± 0.2 ± 0.01 ± 0.05	> 0.84 mm - 0% > 0.60 mm - 1% max < 0.125 mm - 1% max
Nepheline syenite	Al_2O_3 > 22.0 SiO_2 < 62.0 Alkali > 13.0 Fe_2O_3 < 0.10	± 0.5 ± 0.5 ± 0.05	> 0.84 mm - 0% > 0.50 mm -3.5% max < 0.1 mm - 20% max
Limestone and dolomite	CaO+MgO > 54.0 Al_2O_3 < 0.3 Fe_2O_3 < 0.10 Rest is CO_2	± 0.1 ± 0.005	> 3.15 mm - 0% > 2.0 mm - 10% max < 0.1 mm - 20% max
Soda ash	Na_2CO_3 > 99.0 NaCl 0.05-0.20 Fe_2O_3 <0.001		> 1.19 mm - 0% > 0.59 mm - 3% max < 0.074 mm -3% max

Batch preparation

Industrial batch preparation

- The different ingredients/raw materials are mixed together in the proper proportions. This mixture of raw materials is called **batch**.
- Normally it is a **powder batch**. In some situations the powder batch is compacted (into **granules or pellets**) before charging into the furnace.
- A normal batch does not include pelletized materials or cullet. However, today cullet recycling (internal and external – post-consumer waste glass) is very common in the glass industry
- Many criteria have to be considered when preparing an industrial batch. Following is a general survey.

Batch calculation

- For each raw material, the concentration of the **relevant oxides** and impurities (Cl, F, S, iron oxides) should be determined

- Many raw materials contain carbonates and nitrates or water. These components dissociate at higher temperatures into oxides and volatile CO_2, NO_2 and H_2O, which evaporate from the batch. This is called **melting loss.** They have to be accounted for

- Other important factors to consider include:
  - ✓ Moisture content of the different raw materials
  - ✓ Evaporation (some components are volatile and will evaporate from the melt, e.g. alkali oxides)
  - ✓ Dispersion (carry-over)
  - ✓ Dissolving refractory
  - ✓ Cullet composition (it may differ from the composition to be produced)

Example – oxide content in raw materials

TABLE 7-1 Glassmaking Materials

Raw material	Chemical composition	Glassmaking oxide	Percent of oxide
Sand	SiO	SiO_2	99.8
Soda ash	Na_2CO_3	Na_2O	58.5
Limestone	$CaCO_3$	CaO	56.0
Dolomite	$CaCO_3$–$MgCO_3$	CaO	30.5
		MgO	21.5
Feldspar	$K_2(Na_2)O$–Al_2O_3–$6SiO_2$	SiO_2	68.0
		Al_2O_3	18.5
		$K_2(Na_2)O$	12.8
		SiO_2	68.0
Nepheline	$NaAlSiO_4$	SiO_2	60.6
Syenite		Al_2O_3	23.3
		$Na_2(K_2)O$	14.8
Borax, 5-Mol	$Na_2B_4O_7$–$5H_2O$	Na_2O	21.8
		B_2O_3	48.8
Boric acid	H_3BO_3	B_2O_3	56.3
Litharge	PbO	PbO	99.9
Potash, anhydrous	K_2CO_3	K_2O	68.0
Fluorspar	CaF_2	CaO	69.9
		F^-	47.1
Zinc oxide	ZnO	ZnO	100.0
Barium carbonate	$BaCO_3$	BaO	76.9

G. McLellan and E. Shand, Glass Engineering Handbook, 3rd edition, 1984, Ed: McGraw-Hill Book Company

One word on REDOX

- **Redox** = Equilibrium between all oxidizing and reducing species in the system
- **Redox** = The ratio of oxidized forms versus reduced forms characterize the oxidation state ("redox")
  - ✓Reducing agents consume oxygen → reduces melt
  - ✓Oxidants deliver oxygen → oxidizes melt

- Redox state of glass <u>*batch*</u> characterised by:
  – Batch redox number (e.g. according to Simpson)
  – Chemical Oxygen Demand (COD)=CSB
- Redox state of glass <u>*melt*</u> characterised by partial oxygen pressure: $pO_2(T)$
- Redox state of glass <u>*product*</u> characterised by for instance the iron redox ratio: Fe^{2+}/Fe_{tot}

Batch redox number

- Important in the calculation procedure for a batch composition, is the **batch redox number**.
- This number characterizes the balance between reducing (oxygen consumers) and oxidizing (oxygen suppliers) species in the batch.
- A high positive redox number of a batch indicates a batch with high oxygen potential: oxidized glass (e.g. iron mainly in Fe^{3+} state)
- The redox state of the batch and of the glass melt will have a strong influence during the melting and fining processes (gas release behavior), as well as on the final properties of the glass (notably color, see next slides). It must be controlled.
- Oxidizing agents (e.g. nitrates) or reducing agents (e.g. cokes) can be added to the batch to adjust the batch redox

Redox number determined by oxidizing or reducing species in batch

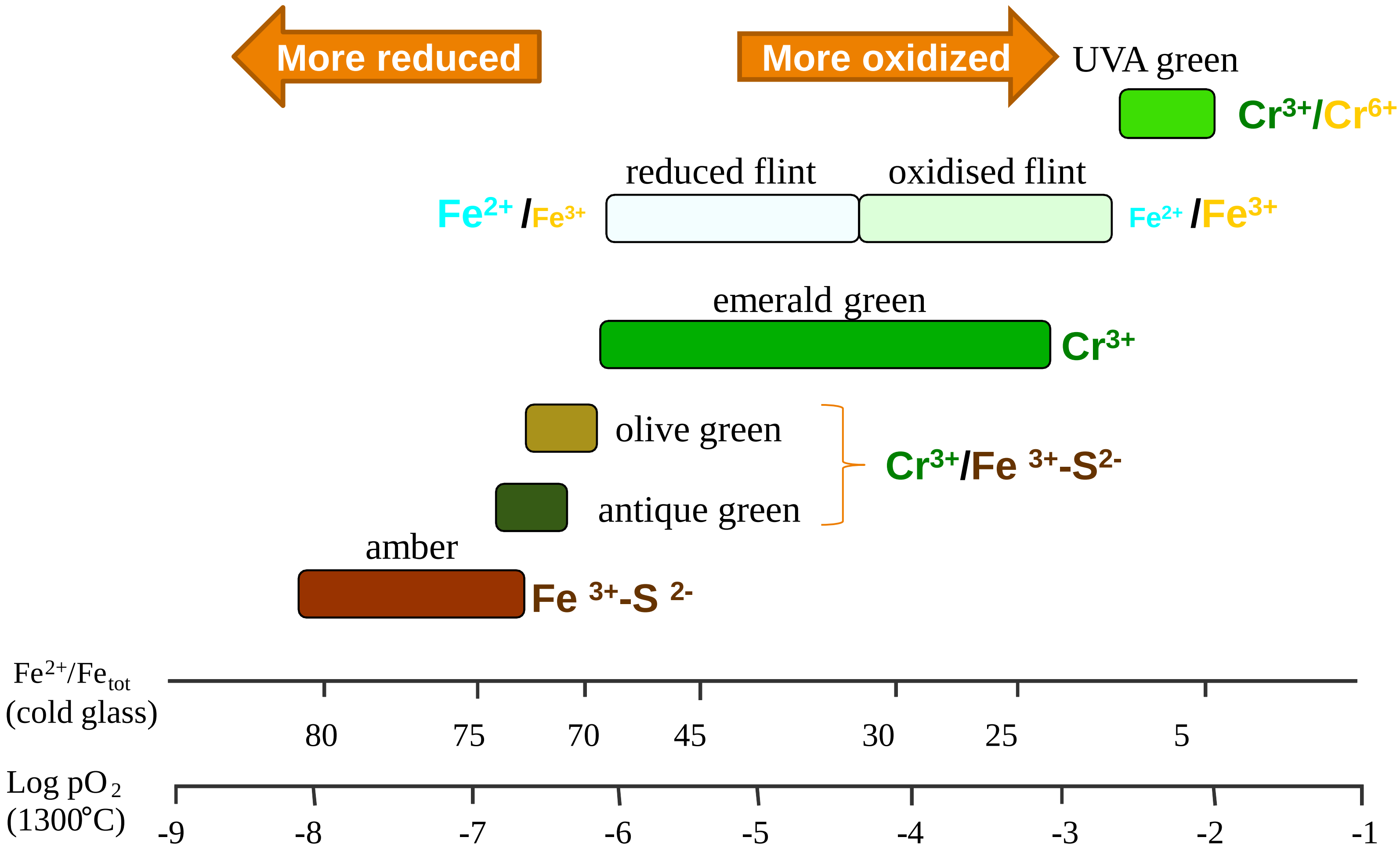
$$R_{total} = \Sigma R_i \cdot G_i$$

G_i reducing or oxidizing compound per 2000 kg sand in batch

R_i redox factor (negative for reducing compounds e.g. carbon)

$R_{batch} = \Sigma R_i G_i$ Gi = weight of component used per 2000 kg of sand	**redox factor R_i**
Oxidizing components	
Sodium sulfate	+ 0.67
Gypsum ($CaSO_4.2\ H_2O$)	+ 0.56
Anhydrous gypsum ($CaSO_4$)	+ 0.70
Barite ($BaSO_4$)	+ 0.40
Sodium nitrate	+ 0.32
Manganese dioxide	+ 1.09
Iron (III) oxide (Fe_2O_3)	+ 0.25
Fe_3O_4	+ 0.19
Reducing components	
Carbon	- 6.70
Cokes 85 % C	- 5.70
Iron sulfide (FeS)	- 1.60
Pyrite (FeS_2)	- 1.20
Fluorspar (CaF_2)	- 0.10
Arsenic oxide (As_2O_3)	- 0.93
Blast furnace slag	- 0.071 till - 0.09
Mellite 40 (iron aluminum silcate)	- 0.10

Redox vs. color of Fe & Cr-containing glasses



From P. Laimbock, ReadOX & Consultancy, presentation at ICG meeting Eindhoven april 2013

Example of batch calculation

Example of batch calculation, assuming 50 % SO_3 retention				
Ingredient	**Amount (gram)**	**Oxide mass fraction**	**Mass in glass (g)**	**Oxide in glass**
Sand	1000	0.98	980	SiO_2
	1000	0.00025	0.25	Fe_2O_3
Soda ash	370	0.585	216.4	Na_2O
Sodium sulfate	4	0.437	1.7	Na_2O
		0.563	0.5 x 2.25*	SO_3
Dolomite	200	0.310 0.210	62 42	CaO MgO
Borax	30	0.365 0.163	10.9 4.9	B_2O_3 Na_2O
Feldspar	55	0.180 0.130 0.680	9.9 7.1 37.4	Al_2O_3 K_2O SiO_2
	1659 g batch		1373.6 g glass	

Melting loss 1659 g - 1373.6 g = 285.4 g = 17.2 % of the batch
Glass composition: 74.1 SiO_2 ; 16.2 Na_2O; 4.5 CaO; 3.1 MgO; 0.8 B_2O_3; 0.7 Al_2O_3; 0.52 K_2O; 0.08 % SO_3 0.02 % Fe_2O_3 (all in mass %)
Sulfate retention assumed to be 50%

Example of batch calculation

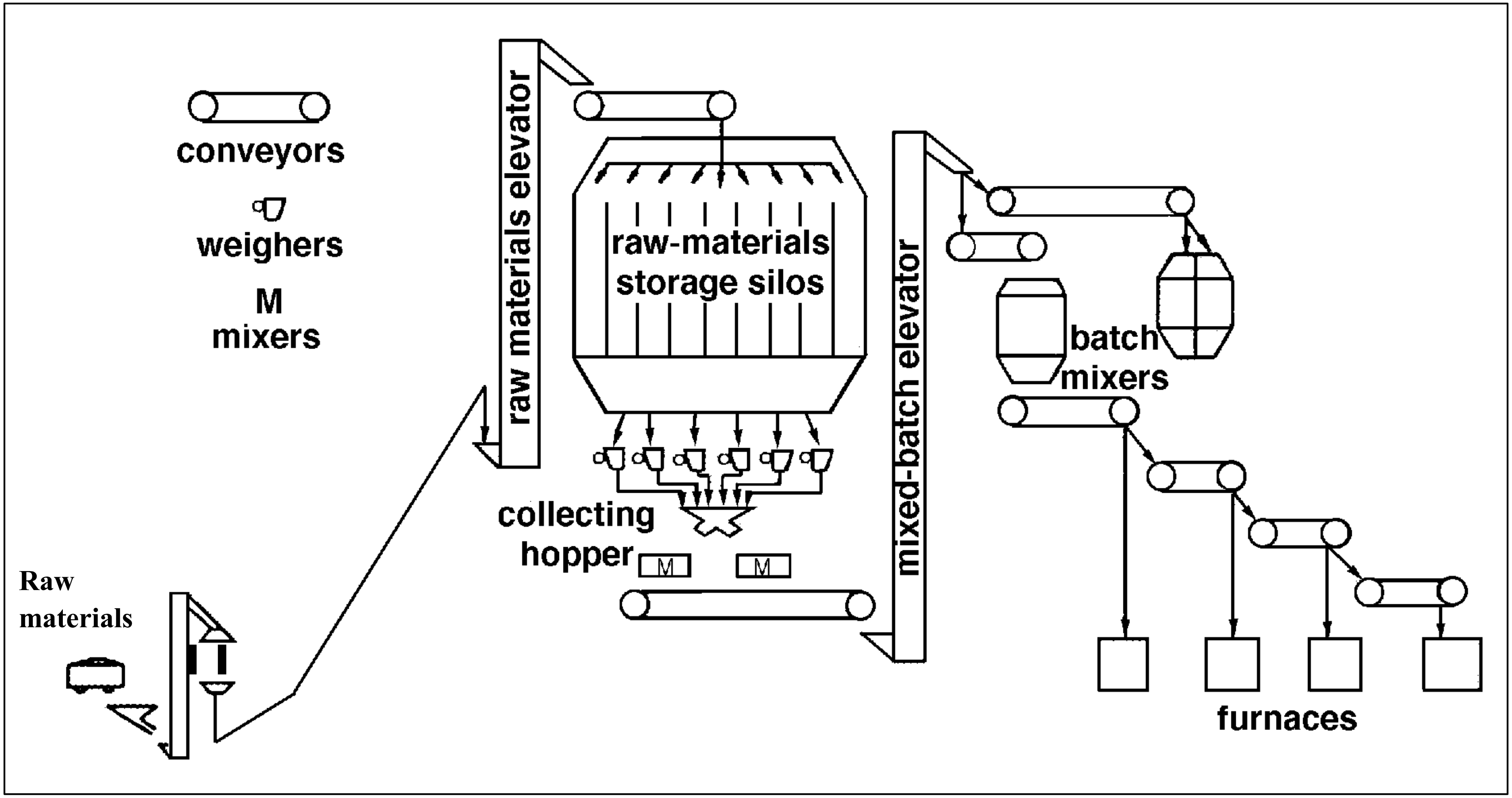
- Reminder: Many raw materials contain carbonates and nitrates or water (hydrated compounds / OH-groups). These components dissociate at higher temperatures into oxides and volatile CO_2, NO_2 and H_2O, which evaporate from the batch. This is called **melting loss**
- For container glass raw material batch, the amount of **dry normal batch** is about **1170 to 1190** kg per 1000 kg molten glass
- For soda-lime-silica float glass, about 1200 -1220 kg dry normal batch is needed to melt 1000 kg glass. The difference is the loss by batch gases.

Industrial batch preparation – Important steps

1. Extraction (or mining) of mineral raw materials or ores and chemical processing for synthetic raw materials
2. Pre-treatment (partly by raw material supplier) or purification and sieving/size classification
3. Shipment to the glass plant
4. Delivery checks on purity, chemical composition, grain size and moisture content
5. Storage in silos
6. Weighing
7. Mixing
8. Conveying to the furnace or day-hopper
9. Feeding batch into the furnace

Industrial batch preparation

- All steps must be controlled, from the raw materials delivery to the charging of the batch into the furnace



Shipment to the glass plant – Delivery checks

- To ensure a stable production, it is important to ensure a continuous, stable and reliable delivery of the raw materials to the glass plant
- Most raw materials are **delivered in bulk** by truck, ship or railroad transport. They are mainly in granular or powder form
- Precautions must be taken to **avoid any contamination** of the raw materials during the delivery (e.g. shipment in poorly cleaned trucks, abrasion during transport...)
- Upon delivery, the glass producer must carry **out inspections on the quality** of the raw materials (composition, impurities, grain size, moisture of the raw materials...), and in case necessary, adjust the batch composition

Storage

- Before the batch preparation, the raw materials must be **stored in the vicinity of the furnace**
- To avoid any disruption in the glass production (e.g. in case of problems with the delivery chain), it is recommended to store enough raw materials to ensure 4 to 5 days of production
- A moder batch house is equipped with different **silos** for the individual raw materials.
- Special care must be taken during charging and discharging from the silos (avoid blowing off of fine particles, avoid segregation, control of the pressure inside the silo)
- Preferably, both coarse and fine particles should be evenly distributed in the silo, and segregation should be avoided

Batch weighing

- **Weighing accuracy** is very important and must be well controlled and calibrated regularly

- Different weighing technologies exist (mobile scales moving from silo to silo, fixed scales)

- Weighing capacities may range from 3500Kg (sand) down to a few hundreds of grams (coloring agents)

- During the weighing cycle, the level of varying water content in the raw materials should be taken into account (especially if wet sand is used) and corrected in the batch composition

- The humidity of the sand can be measured using dedicated systems (based on neutron absorption, microwave measurement of infrared)

Batch mixing

- The **homogeneity** of the glass produced is strongly determined by the homogeneity of the batch. **A good mixing is essential**

- Industrial glass batches are mixed into portion of up to 4000Kg. It may take place either dry of with some addition of some water (for segregation)

- Often the raw materials with only small weights in the batch are mixed together separately or with some sand. This is called a premix. The premix with different (small amounts) batch ingredients can then be dosed to the main batch.

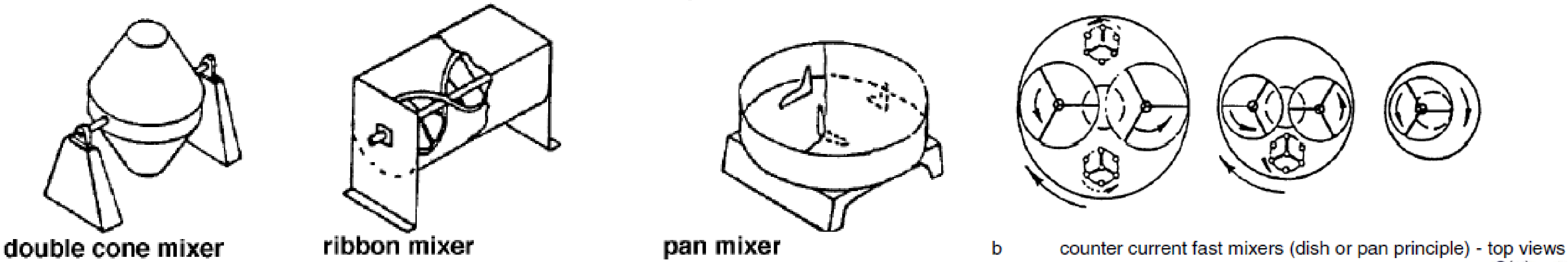
- Typically, 10 batches per hour are prepared by one mixer

- The batch homogeneity can be measured by taking several samples of batch and analyse its composition (e.g. with XRF)

Batch mixing

- Water may be added to the batch preferably above 36°C to avoid hydration of soda. The added water is weighed before addition to the batch (taking into account the water content of cullet and sand)
- The quantities of water addition to the batch need to be limited: The evaporation of batch water in the glass furnace requires a very high quantity of extra energy.
- Cullet is added to the batch just before the end of the mixing cycle or even afterwards during the emptying of the mixer in order to prevent wear of the mixer.

Some examples of batch mixers



Briquettes / pellets

- Before introduction in the furnace, the batch may be pre-treated to produce **briquettes, pellets or granules**
- These present **numerous benefits** (avoid segregation of the batch, faster melting, energy savings, better glass homogeneity) but require **extra investments and lead to higher raw material prices**

Read more:

M. Rongen et al, “Advantages of pelletized raw materials”, 23rd ICG conference, Prague, 2013 (available online)

Batch conveying

- It is very important that a well-mixed batch does not segregate during transport like conveying. The **transfer distances** between the mixer and the batch charger at the furnace should **be as short as possible**.

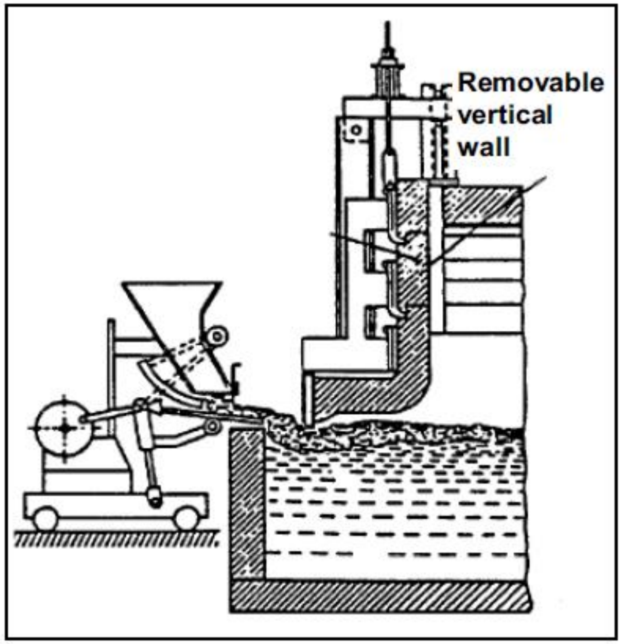
- Addition of a few mass percent of water (2 to 4 %) will restrain the segregation very effectively, but it may also create problems with hygroscopic raw materials like soda ash.

- Conveying of batch can take place with transport belts, via screw conveyors for transport across short distances (for instance for tacky material) or through vibrating ducts. Pneumatic transport can be used for the separate ingredients (raw materials).

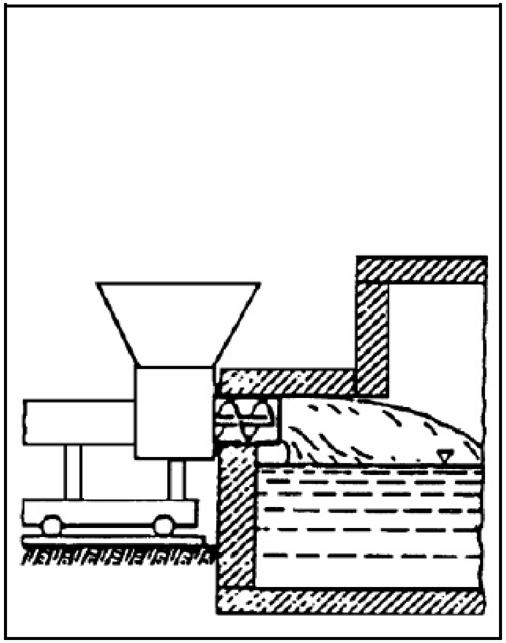
- Pneumatic transport is often used for very fine batch materials such as for E-glass fibre production (continuous filament glass fibres).

Batch feeding

- The batch is introduced into the glass melting tank via one or several so-called "**doghouse**" or "**day-hopper**" (at back or side of the furnace)
- The charging of the batch may occur by means of screw conveyors, vibrating plates or scrapers (mostly used)



Batch charging into open doghouse by a pusher mechanism



Batch charging into closed doghouse using a screw charger

Batch feeding

- Charging of the furnace by batch is controlled by using glass melt level probes (can be Pt-electrodes, optical measurement…)

- Preferably a thin **batch blanket** is supplied on top of the glass melt in a melting tank, in order to obtain a relatively fast melting rate. A thick batch blanket on top of the molten glass will limit the heating rate of the inner layers of this batch.

- Depending on the charging method, the batch can float as a continuous **blanket layer** on the melt or may be moving as **islands** (which is generally the case with container glass furnaces) over the melt.

Conclusions – 1/2

- Glass is everywhere. There is a multitude of applications of glass, and of types / compositions of glasses
- The **glass composition** is chosen as function of the **required properties**, but also **technical and economical aspects**
- The **choice of the raw materials is crucial**, as it not only determines the final composition of the glass, but also has a tremendous impact on the melting process (and on the costs involved)
- The exact composition of the raw materials has to be taken into account, especially the **redox**, the impurities and contamination, but also grain size distribution, the necessity for pretreatments…
- **Good raw material selection** is one of the key for successful industrial glass production

Conclusions – 2/2

- Industrial batch preparation requires a series of steps to follow to ensure the production of a good product, and each one requires **good control**

- **Homogeneity of the batch** preparation is another key in the glass production. Efficient raw materials transport, storage, weighing, mixing and conveying to the furnace are of utmost importance.

- All along these steps, the glass producer must **avoid as much as possible all contaminations**, which bring instabilities and/or damages in the production process

- The technical considerations presented so far brought us from the source of the raw materials to the introduction of the batch in the furnace. Many more processes take place and many technical aspects have to be considered until the final glass is produced. These will be seen in the next lectures…

References and further reading

- Book “Introduction to Glass Science and Technology”, J. Shelby (RSC publishing, 2nd edition 2005)
- Book “Fundamentals of Inorganic Glasses”, A. Varshneya (Elsevier, 1993)
- Glass Technology journals (e.g. European Journal of Glass Science and Technology)
- NCNG’s Glass Technology course and handbook 2013
- Proceedings of GlassTrend meetings and seminars (www.glasstrend.nl)
- Proceedings of “Glass Problem Conferences” (Wiley, every year)
- Youtube video: Production of Glass Bottles - How it's made

Home assignment

- A multiple choice questionnaire (MCQ) including questions on glass compositions, raw materials and industrial batch preparation is provided with this lecture
- The MCQ will be available online on IMI's website

Thank you for your attention

Questions ?

Visit us in Eindhoven

Contact me via email:

mathieu.hubert@celsian.nl