Lecture 8.

RAW MATERIALS FOR GLASS MAKING

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The principal oxides present in commercial flat glass and container glasses are:

SiO_2 Na_2O CaO MgO Al_2O_3 refining agents, colorants

in approximately decreasing order of content. In other systems PbO, B_2O_3, K_2O, ZnO, BaO and F may also be present. All are used for the effect they have on particular physical and chemical properties and in what follows you will learn more about their roles. Before discussing their effect on properties we examine the forms in which these raw materials are available because this can constrain our freedom to design a particular glass composition; e.g. there are significant cost variations between different raw materials and batch costs can be 20% or more of total glass manufacturing costs. The subject of raw materials will be examined in more detail in the Raw Materials Module.

In selecting materials for glass making the following considerations are important:

a) availability
b) cost of purchase and transport
c) security of supply
d) melting characteristics
e) grain size distribution
f) long term stability (e.g. tendency to hydrate)
g) purity
h) effect on equipment life
i) environmental considerations, toxicity, dust forming characteristics

Some of these factors are of course related e.g. d) to e), e) to h) and i). Purity levels relate to cost, certain impurities may be desirable while others are only tolerable at very low levels; one refractory mineral grain (2mg wt.) may cause problems if present at the level of 1 per container (300g). g) and i) may be subject to British Standard requirements or environmental legislation.

Silica is available naturally and in abundance as sand, but only in a few sites have geological factors led to a close to ideal grain size distribution, i.e. a tight distribution around a size of 0.4mm. Large grains (>1mm) melt too slowly, while fine dry grains cause dusting during handling which is a pollution hazard and increases wear in the furnace combustion space. Grinding and sieving to improve the grain size distribution adds cost. Many sands are contaminated with iron bearing minerals that discolour the glass and, if poorly controlled, can lead to varying heat transfer conditions in the melt, so upsetting flow patterns. For optical quality glasses tight requirements on colorant impurity levels must be imposed e.g. <0.008% Fe, 0.03% Ti and 2ppm Cr (BS2975). Requirements for tableware are almost as rigid; for example the sand used for lead glass should have

<0.013% Fe whereas flint container glass can contain as much as 0.03 wt % Fe and flat glass up to 0.1% Fe. Amber glasses have 0.3 % Fe because the Fe is used as a colorant. While flat glass producers can tolerate higher iron levels than tableware producers they require a consistent supply otherwise heat transfer characteristics (and hence flow patterns) in the melt can be affected.

Other impurities may also be important. For example sand for photomultiplier tube manufacture must have K_2O <0.05 wt %. This is because of the radioactivity of one of the potassium isotopes. Similarly levels of uranium and thorium must be well below those present normally in the environment. In another case production of SiO_2 tubes with less than 0.1 wt% Na_2O was interrupted when the supplier started to wash his sand in sea-water and the Na_2O content rose to 0.4%.

Other contaminants include refractory grains rich in such oxides as alumina, chromic oxide, or zirconia. Sources of good quality glass making sands are therefore limited to just a few sites in Britain and even then mechanical processing is necessary to minimise contamination and to ensure a properly graded product. Because one processing step involves washing, sand is normally delivered wet and contains about 8 wt. % moisture. Some of the water is lost by drainage during storage but normally wet sand (3-4% water) is used in the batch and a correction must be made for the level of water present. Wet batch reduces segregation and dusting during handling but uses energy for its evaporation and reduces control of batch composition unless accurately monitored. Controlled drying may therefore be adopted in some plants.

Sodium oxide cannot be used as a batch material because it is highly hygroscopic. A number of sodium salts are available as a source of this flux including the carbonate, chloride, sulphate and nitrate. The latter three cause pollution problems on decomposition and an excess of sulphate is insoluble in the glass melt so causing a defect called gall. As a partial source of sodium however both sulphate and nitrate are occasionally used, the former to aid refining and accelerate melting, while the latter acts as an oxidising agent controlling batch redox and has been used in combination with arsenic to aid refining.

Carbonate is the main source of sodium however. This is relatively expensive but readily available and is reasonably stable in normal atmospheres. If subjected to high humidity levels under warm conditions in well-ventilated sites for long periods absorption of water and CO_2 can occur, so causing weighing errors. Sodium carbonate in the UK is produced chemically from salt and may still contain small proportions of chloride, but is available in some countries as a raw material produced by lake evaporation and then may be effectively chloride free. The latter is a cheaper source and is providing downward pressure on the cost of the former. Processing can produce a reasonably dense grade of anhydrous sodium carbonate (1g/cm^3) with a grain size matched to that of the sand. Potassium carbonate is used in crystal glass manufacture.

Alkali earth oxides are also introduced as carbonates although occasionally calcium sulphate (gypsum) can be used. Calcium and magnesium carbonates occur naturally as limestone ($CaCO_3$) and dolomite ($CaCO_3.MgCO_3$). Both are available at low cost. Low Fe limestones are available in the UK; dolomite is imported. In TV tube glass manufacture $BaCO_3$ is used to improve electrical resistance; for similar reasons Na levels are minimised (<0.1wt %). One supplier ran into problems however as a result of using Na_2CO_3 to precipitate $BaCO_3$ from a Ba rich solution rather than CO_2.

Alumina bearing minerals are not cheap, they are often relatively refractory and may be contaminated with significant iron levels. They must therefore be chosen with care. There is often a low level of aluminous material as a contaminant in sand and this may be advantageous since sand is cheaper than alumina bearing minerals. Felspathic and felspathoid minerals, e.g. nepheline syenite ($NaAlSiO_4$), melt at low temperatures but can produce viscous knots in the glass if too coarse. An important source of alumina is blast furnace slag sold as a commercial product. This contains calcium and magnesium aluminosilicates and can replace up to about 7% of the sand in flint glasses. Its advantages include action as a melting accelerator and as an aid for refining.

Lead oxide for crystal glass manufacture is normally supplied as red lead (Pb_3O_4) and requires careful handling in sealed systems. Lead silicate can reduce volatilisation during early stages of melting, and is easier to handle.

Boric oxide is often supplied as borax ($Na_2B_4O_7.10H_2O$), as rasorite (a crude sodium borate) or, for Na free borosilicate glass, colemanite ($Ca_3B_6O_{11}.5H_2O$).

Other raw materials are: Na_2SiF_6, CaF_2, ZnO, colorants such as Se, CoO, Cr_2O_3, NiO, FeS and refining agents e.g. As, Sb (both rarely used now), sulphates, chlorides, fluorides.

In-house and foreign cullet also provides a major resource at levels between 10 and 60% and even occasionally up to 100% of batch. This raw material can also be seriously contaminated with other coloured glasses, components only poorly soluble in the glass tank, and species such as lead which can have implications in terms of environmental legislation.

In designing glass batches and glass compositions the size of the batch house available may be a significant limiting factor in the number of separate components, since only a small number of silos may be available and two of these may contain sand. For minor components such as colorants this is a less severe limitation since they are normally premixed.

Accurate control of glass quality and composition requires careful attention to detail such as batch component water levels, weighing errors, contaminant levels (in house as well as in delivered materials) closed circuit delivery systems and interlocked silo filling systems to avoid incorrect loading. Good batch mixing and transport systems that avoid segregation are also vital.

Example batch calculation.

Calculate in wt % the composition of glass made by melting the following raw materials together: 18 kg sodium carbonate; 14 kg limestone; 50 kg of sand; 2 kg of aluminium hydroxide. [14 marks]

(Relative Molecular Mass (RMM): $Na_2O = 61.98$;$CaO = 56.08$; $SiO_2 = 60.08$; $Al_2O_3 = 101.96$; $CO_2 = 44.01$; $H_2O = 18.01$)

$$Na_2CO_3 \rightarrow Na_2O + CO_2$$

105.99 (i.e. 61.98+44.01) kg of Na_2CO_3 gives 61.98 kg of Na_2O and 44.01 kg of CO_2

So 18 kg of Na_2CO_3 gives 18*61.98/105.99 kg of sodium oxide = 10.53 kg

$$CaCO_3 \rightarrow CaO + CO_2$$

14 kg of $CaCO_3$ gives 14*56.08/(56.08+44.01) kg of CaO = 7.84 kg

50 kg of sand gives 50 kg of SiO_2

$$Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

2 kg of aluminium hydroxide gives 2*101.96/(101.96+3*18.01) = 1.31 kg of alumina

Total mass of glass = 10.53 + 7.84 + 50 + 1.31 = 69.68 kg

Therefore composition in wt % is:

15.11 wt % Na_2O; 11.25 wt % CaO; 71.76 wt % SiO_2; 1.88 wt % Al_2O_3

To calculate the glass composition for the case where the raw materials include a range of components need to set up a matrix with oxide components and raw materials as x and y components.

The viscosity of the glass can be expressed by means of the Fulcher equation:

$$\log h = -A + \frac{B}{T - T_0}$$

with A =1.3991; B = 3879.96; T_0 = 288.96.

On re-arranging above equation and setting $\log\eta$ =13, glass transition temperature = 3879.96/(13+1.3991) + 288.96 = 558^{0}C.

Relationship between minor components and glass composition/properties.

The following factors can affect the glass composition and make it different to anticipated composition:

1) Water in batch. For example sand is often supplied wet. After storage the water content may fall but there is ultimately some advantage in using a slightly wet batch, in that segregation is reduced as is dusting in the furnace space. Short of drying the raw materials and adding a known amount of water, the water content of sand (and any other wet material) must therefore be monitored.

2) Impurities such as iron will affect glass colour. They can also influence heat transfer in the melt because they affect absorption in infrared, and hence upset flow characteristics if allowed to vary. In amber glass Fe_2O_3 levels are around 0.3 wt%, in float around 0.1 wt%, containers 0.03 wt%, crystal 0.013 wt%.

3) aluminous impurities if present as refractory aluminous minerals can ultimately lead to stones since they may not disperse completely on passing through the furnace. Some remain as crystalline defects, others may melt but be too viscous to disperse.

4) there will be a certain level of contamination from dissolved refractories in the glass. In particular the ZrO_2 content is likely to be slightly enhanced since most glass contact refractories are fused cast AZS. This

does not normally cause a problem but can do so if the corrosion products do not mix thoroughly with the glass but instead form a localised defect.

5) volatilisation can lead to the loss of oxides such as Na_2O, PbO, B_2O_3, or other species such as Se, F. Indeed only 10% of added Se may remain in glass. In the worst cases such volatilisation can lead to a depleted, SiO_2 layer on the melt surface, which may subsequently devitrify and give rise to defects.

6) glass redox can be affected by melting conditions such as furnace atmosphere, reducing agents in batch. This in turn can affect glass colour, refining. Premature reduction of sodium sulphate can also reduce its effectiveness as a stirring agent in the melt and can lead to silica stones.

7) Oxyfuel firing is leading to furnace atmospheres which contain 4 times the concentration of H_2O. Since the hydroxyl content of the glass varies as $\sqrt{(H_2O)}$ it will therefore be twice as high as normal. Concentrations may approach 0.1 wt%. Hydrogen behaves in an analogous fashion to Na i.e. as a network modifier but is much more effective on a wt per wt basis because of its lower atomic number, and also because of its exceptional ionic radius. Producers melting glass under these conditions report enhanced refining and homogenising rates and higher % pack rates.

Conclusions

From the text and the table it should be clear that choice of batch materials is a balance between cost, melting rates, purities, safety and choice of composition with correct physical and chemical characteristics. The minor impurities in the batch can play a significant role in the physical properties of the glass produced particularly in the case of specialist products.

Table 1

Principal properties of different batch components. Proportions given refer to commercial flat and container compositions. For glasses used for other purposes compositions may differ significantly and the rôle of the oxides may not be quite the same:

SiO_2	Glass-former. Increases viscosity, durability, melting times and refining times. Lowers expansion coefficient, density, refractive index. (container and flat glass: 73%)
Na_2O	Flux. Lowers viscosity, melting times, refining times, durability. Increases expansion coefficient, density, refractive index. (typical level 12-14 wt.%)
CaO	Flux. Lowers viscosity at high temperatures but increases it at low temperatures. Improves durability. Increases expansion coefficient, density, refractive index. Too much lowers glass stability. (typically 11 wt.%)
MgO	Similar to CaO but lowers liquidus temperatures when replacing CaO. Above about 3% can start to increase crystallisation rates again. Can improve durability. Does not steepen the temperature-viscosity curve to same extent as CaO. (<4%)

Al_2O_3	At lower levels acts as a network former cf. silica. Improves durability, stability against devitrification. Decreases expansion coefficient. (<2%)
B_2O_3	In small quantities can act as a flux while reducing expansion coefficient, improving durability and lowering refractive index.
PbO	Used to give high refractive index and dispersion. Gives low melting point glasses with high electrical resistance.

Bibliography

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