

Glass Redox

Glass Redox can be defined simply as the reduced or oxidised state of a glass. It is affected by the cullet composition, the furnace atmosphere, the batch composition, the thermal history of the glass, etc.

This reduced / oxidised condition in general determines the level of sulphate as SO₃ retained in the glass. A highly oxidised glass will contain as much as 0.30% SO₃ whereas a highly reduced glass may contain as little as 0.025% SO₃.

The lower the glass redox, the lower the solubility of SO₃ in the glass and, therefore, the glasses which lose more SO₃ and / or retain less SO₃ will be better refined. When released out of the glass it is in the form of SO₂.

SO₃ Retained in Glass	Colour
0.30	UVA Green
0.20	Oxidised Flint
0.15	Reduced Flint
0.10	Emerald Green
0.025	Amber

This better refining, which is generally obtained at a lower redox, also allows the furnace to be run at a slightly lower temperature using less fuel.

Batch Redox Concept

To enable predictions to be made of the glass redox an empirical method of calculating the batch redox was developed by The Calumite Company, USA. By assigning factors to each of the batch materials that may affect the redox state, a total redox number can be calculated for each batch. Reducing materials include Carbon, Anthracite, Iron Pyrites, Iron Chromite, sulphide sulphur from beneficiated slag - with factors ranging from minus 0.10 to minus 9.00. Oxidising material include Sodium Sulphate, Cerium Oxide, Iron Oxide, Sodium and Potassium Nitrate – with factors ranging from +0.19 to +1.20.

Note: a particular composition’s total batch redox number is very useful when altering the batch or glass in that particular furnace. To duplicate the glass in a different furnace the composition gives a good starting point but may need to be altered due to the different furnace conditions.

The total batch redox number is indicative of the resultant oxidation / reduction state of the glass being produced. This is particularly valuable when colour changes are made in the furnace.

Typical Batch Redox	Colour
20+	UVA Green
5 to 20+	Oxidised Flint
1 to 5+	Reduced Flint
+1 to -10	Emerald Green
-20 preferably -25 to -30	Amber

glass to the blue-green (ferrous iron) glass. For this reason some companies will produce their flint glass from higher redox batches.

For factories using selenium (adding a pink to physically decolourise, or mask, the iron from lower iron sands) it will be better for them to work at a lower redox where the selenium will not oxidise to its colourless state.

Decolourisation of colour (decolorising) - It is extremely difficult to attenuate the green tint created in glass by chromium oxide, usually originating from sand and other minerals and so we will concentrate on the colour produced by iron.

The physical method of decolourising has been to introduce a complimentary colour of pink from selenium and blue from cobalt oxide to counter the various shades of green produced by iron. Obviously, as more masking decolourisers are added to the glass the more it will become grey and lose its brightness.

Iron in the ferric state is a yellow-green and is less intense the blue-green ferrous iron. In the past the tendency has been to oxidise the glass to the ferric state so that the less intense colour could be more easily masked by selenium. However, selenium if highly oxidised becomes colourless.

Decolourising reduced flints with lower levels of beneficiated slag has not presented greater problems. In a reduced glass there is an increased retention of selenium in the glass and also it has remained in the pink state. Often the presence of the slag enables a lower temperature to be used enabling the selenium to be more effective. Therefore, despite a relatively more intense iron colour, no more selenium is usually required.

There has been a trend towards using cerium oxide in cosmetic ware and table ware glass as it changes the valent state of the iron to a colourless form. In most of these situations 1 to 2kg of cerium oxide for every 2000kg of sand is usually sufficient. (At the 2kg level it also reduces UV transmission to less than 20%) The use of cerium with low levels of selenium is not advantageous as it can oxidise the selenium to its colourless state.

When attempts are made to decolourise higher levels of iron with high levels of selenium the melting conditions need to be carefully controlled or grey-green selenides can be formed.

Reducing the level of iron in the melt through careful magnetic separation and washing of the cullet, assessing alternative sands, calcium sources and alumina sources (i.e. calcined alumina) may be effective in producing a premium priced product.

Glassworks Services Limited will give customers help in refining, melting, colour, and colour changes based on the information provided by the customer regarding available materials local to them and their original batch composition.

Amber Glass and redox

The amber chromophore has been shown to be a tetrahedrally co-ordinated ferric ion, with one sulphide and three oxygen ligands. Therefore there are limits of redox state, which must be observed, for the amber glass formation:-

- if the melt is too oxidising there will be an excess of ferric iron and insufficient sulphide;
- if the melt is too reducing there will be insufficient ferric iron and excess sulphide.

The amber formation is affected by:-

- the atmosphere above and within the melt;
- glass composition; the ferrous/ferric ratio;
- the sulphide/sulphate ratio;
- the solubility of sulphate.

The total iron in the glass and the total sulphur in the batch are also important.

It has been found in practice that most container glass compositions that the above requirements are met if the total iron in the glass is 0.25% Fe₂O₃ and sulphide sulphur is added to provide a theoretical sulphide in the glass of 0.065% to 0.075%. Furthermore, the correct oxidation conditions to obtain the correct ferrous/ferric ratio, etc. to provide the normal amber colour required for containers is developed with an approximate -25 / -30 batch redox.

Methods of calculating a batch to suit the above condition are available, in particular to ensure no excess sulphide remains in the glass which would produce a susceptibility to reboil and blister formation and also to allow the use of an iron silicate to give the correct iron content without affecting the redox state.

(Also see Amber Glass)

Green Glass

Emerald Green – Iron chromite is the essential ingredient for making standard emerald green glass. About 6 to 10 kgs of chromite is used per tonne of sand. Ideally the base glass will be a reduced flint glass with a redox of about +5; the added chromite would take the redox to about minus 7. A small amount of anthracite or carbon can be used as a reducing agent to trim and control the colour. To satisfy the customer various colour shades can be produced by adding small amounts of copper oxide, cobalt oxide or nickel oxide.

Iron chromite is often referred to as chrome flour due to the need for it to be 400 mesh or finer (38 micron or lower). If the chromite is coarser it will not melt in the molten glass resulting in black specks (referred to as black stones) in the finished product. If the chrome flour is damp it agglomerates resulting in similar black specs; by mixing the chrome flour with an equal quantity of soda ash (sodium carbonate), which absorbs any moisture, this problem can be avoided.

UVA Emerald Green – This is a highly oxidised glass with the required chrome content normally provided by sodium or potassium dichromate. However, the dichromate is a hazardous material to handle and it would be worthy of consideration to use chrome flour instead. The glass would then have to be a very highly oxidised state to accommodate the reducing nature of the chrome flour. In some cases the iron content of the chrome flour may be a limiting factor in its use in this type of glass. The chrome content of UVA emerald green is about half that of a standard emerald green. Sometimes a little cobalt oxide or copper oxide is used to adjust the green shade.

Georgia Green – This is a pale green required by some drinks manufacturers to give added distinction to their product. A level of chrome flour of one-tenth that used for a standard emerald green is typical.

Dead Leaf Green – This colour can be produced using a combination of chrome flour (about 1 kgs per tonne of sand) and iron pyrites (about 2 kgs per tonne of sand). These quantities and the redox state of the glass can be modified to obtain the required depth and shade of colour. The redox state has to be maintained at a constant level and using anthracite or carbon as the reducing agent achieves this. Similar colours have been achieved using low levels of chromium and manganese oxides. The level of each ingredient will depend on the depth of colour and tint required by the ultimate user.

Amber Glass

Amber glass produced using carbon and sulphur is a most unstable glass susceptible to seed and blister (reboil).

Using iron pyrites is one of the more reliable ways of producing an amber glass. Adding the appropriate amounts of iron and sulphide sulphur in combination at the correct redox forms the amber colour. The amount of iron pyrites used will be approximately 2 ½ kgs per tonne of sand. Normal beer bottle amber will contain 0.25 to 0.30% of Fe_2O_3 and if sufficient iron is not available from the sand and pyrites more can be added using iron silicate or using red iron oxide. Using additional iron pyrites to increase the iron is not recommended, as this will add too much sulphide and an unstable glass will result. A golden amber will contain about 0.15% Fe_2O_3 and dark ambers as much as 0.40%. In some circumstances the dark ambers can be made even darker by using colours at various levels of light transmission i.e. by adding small amounts of cobalt oxide and / or copper oxide.

Where it is economically available beneficiated slag is used. It is composed mainly of calcium, alumina and silica but also contains sulphide sulphur. This is a dilute source of sulphur which can be used as an alternative to iron pyrites in all green and amber glasses – whilst also bringing melting advantages. In emerald green it can contribute about 10% of the batch, compared to the sand weight, and in amber as much as 15%. Using these quantities it can replace the alumina source. Even in flint glasses it contributes about 5%, compared to the sand weight, and in all cases improves both the refining, melting and, consequently, the fuel economy of a furnace.

(Also see [Amber Glass and redox](#))

Colour changes without foaming

Changing from an oxidised glass, such as flint or green, to a reduced glass, such as amber, has historically required the furnace to be drained. Changing from flint to green did not cause any major problems but when changing from glasses of substantially different oxidation states severe foaming was often encountered. No-one wants a furnace full of foaming molten glass trying to force its way out.

The batch redox number concept allows the state of oxidation to be predicted from the batch composition, thus enabling controlled and predetermined changes to be made to the redox state of the glass. Using this approach, when changing from amber to flint, the amber is allowed to become less reduced until it is at its limit of colour stability and quality acceptance (enabling packing of glass until the last possible moment) the glass is then held at this state for a time and then moved through the critical sulphur solubility zone in a series of small changes until it becomes oxidised. Once through this zone it can be changed more quickly to the desired oxidation state of a good flint glass.

The redox number concept enables calculated changes to be made to the batch. At zero redox the sulphur is at its lowest solubility and therefore susceptible to foaming but by controlling the passage through this zone there is less chance of any foam being produced. A similar procedure is used to move from an oxidised glass to a reduced amber. It can enable longer packing before the final change and it usually ensures a quicker and safer changeover time.

(Also see [Batch Redox Concept](#))

Refining – all types of glasses

Soda-Lime - In the past soda-lime glass makers used arsenic trioxide with sodium nitrate as their main refining agents. Later carbon with a “sulphate” was used in addition to, or as an alternative to, the arsenic/nitrate method. The sulphate can be sodium, calcium (anhydrite or andricite) or barium. Currently sodium sulphate (also known as saltcake) is the more economic source

In both cases there was a stirring action in the melt and an improvement in the seed count due to the large bubbles produced collecting, and absorbing, the smaller ones as they moved to the surface. At about 1040°C it collects at the interfaces of the melt between the particles of un-dissolved batch, the gas bubbles and on the surface. It therefore acts as a surfactant and increases the melt fluidity. At about 1288°C the thermal decomposition of the sulphate in the glass becomes significant – ultimately producing a stirring action at the interfaces which accelerates the dissolution of unmelted particles and allows bubbles to rise more rapidly through the melt. When sulphate is decomposed by a sulphide this begins at about 900°C and the reactions mentioned above occur earlier. The most economic source of the sulphide is from beneficiated slag such as the Calumite product. In addition the sulphate-sulphide

reaction causes most of the sulphur in the batch to be ejected as SO₂ thus reducing the possibility of foaming or reboil later in the melting process.

Lead - In refining lead glass melts, in particular with pot melting, the glassmaker traditionally used arsenic trioxide and sodium and/or potassium nitrate for 30% PbO compositions and antimony trioxide and nitrate for lower lead levels. In recent years for environmental and legislative reasons, most glassmakers have changed to the use of antimony trioxide. In practice 15% to 30% of the arsenic introduced into the batch can evaporate from the melting batch in open pots while for antimony the figure is closer to 10%; however, the antimony has a somewhat weaker oxidising effect on Fe than the arsenic.

In the early stages of melting the trioxide changes to the pentoxide taking in oxygen from the nitrate. Small bubbles produced during the melting are difficult to remove however at the later stages of founding when temperatures are being lowered as the pentoxide releases oxygen and reverts to the trioxide. The large bubbles produced collect up the small bubbles present in the melt and take them to the melt surface. The final part of the refining process consists of reducing the temperature of the furnace to about 100oC below the normal working temperature for about an hour before raising again in order to begin work. This final action helps to take any remaining seed into solution.

Devitrification

Devitrification of a glass means that some of the molten glass has crystallized. Corresponding to every glass composition there is a limiting temperature below which, given sufficient time, crystalline material will appear in the glass. This temperature will be constant for any given glass composition. The above limiting temperature is normally referred to as the liquidus temperature. The normal working temperature ranges of commercial tank furnace glasses are comfortably above their liquidus temperatures and devitrification problems are rare.

A glass should be designed so that the production process is complete sufficiently quickly so that the glass passes through the liquidus temperature without allowing the glass time to form crystals. Where it is not possible it is advisable to make sure that the liquidus temperature is quite low through attention to the glass composition. In the production of float glass and tubing, where cooling is relatively slow, some of the CaO is replaced by MgO, or additional MgO is added, thus lowering the liquidus temperature substantially.

The rate of devitrification of glasses tends to increase as the temperature falls below the liquidus temperature however devitrification is opposed by the increasing viscosity of the glass. In a glassmaking furnace the bottom glass will generally be colder than that on the surface. If there are corners with poor glass flow, where the glass is likely to be colder, there is a possibility of “devit” being formed. This can also occur when the tank is nearing the end of its campaign and the glass contact refractories are wearing thin resulting in the adjacent glass becoming cooler than the main glass flow.

Running pots and furnaces at lower temperatures to save on fuel can lead to “devit”. The bigger the difference between the liquidus temperature and the main tank temperature the lower the possibility of devitrification. Increasing the tank temperature or introducing bubblers or boost into colder areas of the tank may be uneconomic and increase refractory wear . A change to the glass composition to lower the liquidus temperature within the constraints of the required working properties and glass/batch cost is the usually the best way.

If increasing calcium to create a quickly hardening glass the likelihood of “devit” increases – magnesia can be substituted as discussed.

It is possible that inadequate mixing or incorrect sizing of batch materials (or segregation due to mixed batch standing far too long) will lead to localised differences in a glass composition with higher than expected liquidus temperature and a possibility of small outbreaks of devitrification. If this occurs in a glass the materials and the standard of mixing should be investigated.