The redox number concept and its use by the glass technologist*

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Factors have been assigned to various batch materials and their subsequent use to establish an empirical redox number of a glass batch is discussed. This redox number can be used to indicate the oxidation–reduction state of any given batch. Various examples are given to show how the glass technologist can utilise this concept on a practical basis within the glassworks.

The main ingredients used for the manufacture of soda–lime glassware, i.e. containers and flat glass, are sand, sodium carbonate, limestone, dolomite, and minerals containing alumina. In addition to colouring agents such as chromium compounds and melting aids such as borates and fluorspar there are two other groups of supplementary raw materials in use; those which have a reducing effect and those which are oxidising.

A paper by Manring & Hopkins[1] first suggested an empirical approach to the use and control of these reducing and oxidising agents and a means of predetermining their effectiveness in the glass melting process. This redox number concept was useful to determine or define the theoretical oxidation–reduction state of a glass batch or furnace. It is not a measure of the free energy state of a raw material in that it would indicate the most effective oxidant to use to oxidise iron in glass (for example, would it be better to use cerium or arsenic oxide?); but it is used to establish the state of a particular melting unit.

Based on both practical experience and written equations, values were assigned to the commonly used oxidising and reducing agents and examples of these are shown in Table 1, each factor being based on the value of 1 kg of raw material per 2000 kg sand in a glass batch.

Table 1. *Redox values of various batch additions*

Reducing agents		*Oxidising agents*	
Sulphide from Calumite slag	−9·00	SO_3 from Calumite slag	+1·20
Carbon from Calumite slag	−6·70	Arsenic	+0·93
Carbon (100%C)	−6·70	Sodium bichromate	+0·77
Coke (85%C)	−5·70	Anhydrate	+0·70
Carbocite (65%C)	−4·36	Salt cake	+0·67
Ferrous sulphide	−1·60	Potassium bichromate	+0·65
Iron pyrites	−1·20	Gypsum	+0·56
Mellite 40 (silicate of iron and alumina)	−0·10	Barytes	+0·40
		Sodium nitrate	+0·32
Iron chromite	−1·00		
Arsenic	−0·93		

The assigned factors in the light of practical experience have in some cases been amended from those stated in the earlier paper. Using these factors a redox number can be assigned to a batch but, dependent on the type of furnace, fuel used, etc., the redox number giving optimum results for any given furnace will vary. This ideal level will be determined after making the necessary adjustments to the batch. Once established, it can be used to indicate the correct level necessary to return to after any other batch changes required for that particular melting unit are made.

Redox number and refining

Because of the sulphide sulphur contained in Calumite slag, it is classified as a reducing agent and, in that rôle, contributes to the reduced–oxidised state of the glass. This reduced or oxidised condition generally determines the level of sulphate retained in the glass. A highly oxidised glass will retain 0·30% or more SO_3, whereas a highly reduced glass will retain as little as 0·02%. Table 2 shows the approximate level of sulphate at both ends of the redox number spectrum, and the glass colours most normally associated with this phenomenon, i.e. the usual level of oxidation–reduction for a particular colour.

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Table 2. *Sulphate level and equivalent redox number for different glasses*

SO_3 retained in glass (%)	0·02	0·05	0·08	0·10	0·15	0·20	0·25	0·30
Redox number	−20	−10	−5	0	+5	+10	+15	+20
Glass colours	Amber (brown)	Blue green	Emerald green		Reduced flints	Oxidised flints		UVA green

As the redox number changes from positive to negative, an improvement in the fining rate of the glass is usually found. This improvement is believed to be due to the reduction of SO_3 retained in the glass. In the case of reduced flint glasses, for example, with more reducing agent available, the retained SO_3 is decreased, thereby making it a better refined glass than that of the highly oxidised flint glasses. It should be noted however that at any given redox number level in flint glass the refining rate is improved by an increased usage of Calumite slag. The effects of Calumite slag and sulphur compounds on refining and melting have been discussed earlier.[2–4]

This better fining action at a lower redox number allows a better quality glass to be produced at a lower melting temperature and fuel usage level. In order to attain a desired redox number the correct amounts of reducing and oxidising agents required must be calculated. To calculate the redox number of a glass batch using factors assigned to these agents, it is important first to put all batches on a common sand base; for ease of calculation, a 2000 kg base has been chosen. Given a batch containing 2000 kg sand, 100 kg Calumite slag, and 20 kg salt cake, the calculation shown below would yield the redox number of + 4·20. It should be noted however that the factor assigned to Calumite slag depends on its source, as slags from different countries and processes can be appreciably different.

Redox calculation

Batch data:	Sand	2000 kg
	Calumite slag	100 kg
	Salt cake	20 kg
Redox contribution:	Calumite slag	100 × −0·0920 = −9·20
	Salt cake	20 × 0·67 = + 13·40
	Redox number	= + 4·20

Actual analytical measurements made showing the effect of changing redox number

As stated above, by varying the redox number one can positively affect the SO_3 retained in a glass. This, in turn, affects the susceptibility of a glass to blister and reboil. A practical example of the effect of a progressive change in redox number on the SO_3 retention in a flint glass is described below.

Calumite slag was introduced into a flint glass stepwise, changing the anhydrite where necessary, to modify the redox number gradually from the original + 16·80 to + 3·72. Samples of bottles produced were retained throughout this period and were subsequently analysed to determine the percentage SO_3 retained. These data, shown in Figure 1, indicate that the retained SO_3 decreased as the redox number decreased—exactly as predicted.

A further example of the effect of varying the redox number of a glass is shown in Figure 2. From the data produced from a series of melts when the redox number was progressively changed and the ferrous–ferric ratio measured, it was apparent that the ferrous–ferric ratio gives an indication of the oxidation state of the glass. On a practical basis, if daily measurements of the ferrous–ferric ratio of a glass are made, and it is found that the ratio is showing a change larger than experimental error would allow,

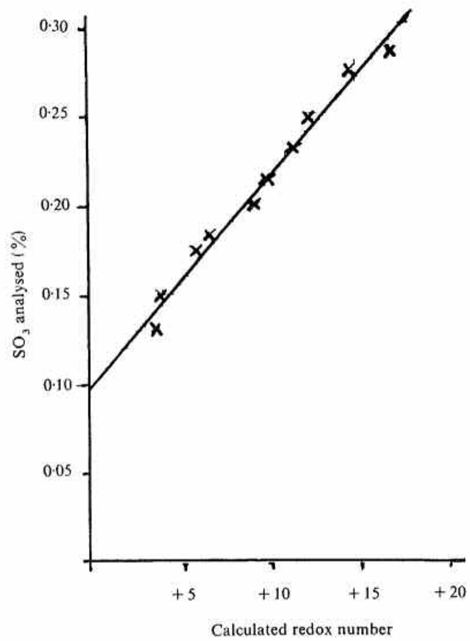

Figure 1. *Relationship between redox number and retained sulphate*

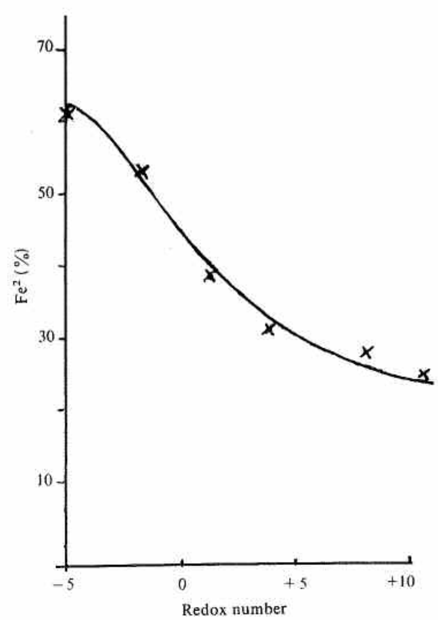

Figure 2. *Relationship between redox number and ferrous-ferric ratio*

it can signify that a change is taking place within the melting unit. However, if a constant redox number has been established for that particular glass and no batch change has been made, then the change may well be in the fuel/air ratio, or other furnace conditions, or possibly due to a raw material being contaminated by a reducing or oxidising agent. An example of the latter will be mentioned later.

Practical use of the redox number concept

Development of batches

Batch changes can be made for a glass, and by using the redox number concept, it enables the glass technologist to maintain the colour in the glass constant, despite major material modifications. In one instance it was considered necessary to introduce Calumite slag into the batch to improve the melting and refining in an amber furnace. The redox number giving the optimum depth of amber colour for American bottles is −24 and this number was therefore maintained throughout the stepwise changes.

The first change was to introduce Calumite slag and remove iron pyrites; it was also considered necessary to increase the iron content of the glass to 0·24%. Therefore, the iron oxide in the batch was increased to compensate for the loss of iron due to removal of the pyrites, plus that necessary to give 0·24% in the glass. The carbon content was reduced to keep the redox number at −24. The second change was to remove all the iron oxide, introduce Melite 40, adjust the other constituents to maintain the same chemical composition, and again modify the carbon content to keep the redox number constant.

Ideally, an amber batch should be designed to work without sulphate, leaving a little carbon to control colour. In this case, due to the large amount of Calumite slag used, it was also necessary to retain a small quantity of sulphate in the batch in order to leave a little carbon for colour control. A fourth change was therefore made to trim back on both the sulphate and carbon, but still keeping the redox number constant. These changes, which were made very successfully with no colour control problems and gave a better melting and refined glass, are shown in Table 3.

Table 3. *Development of an amber batch, retaining a redox number of −24*

Batch components	*Original batch*	*Change 1*	*Change 2*	*Change 3*
Sand	2000	2000	2000	2000
Soda ash	659	683	684	686
Limestone	563	375	375	375
Aplite	201	105	83	83
Calumite slag	—	240	240	240
Salt cake	11	11	11	8
Pyrites	4·29	—	—	—
Melite 40	—	—	22	22
Iron oxide	1·85	5·07	—	—
Carbon (65%)	6·12	1·61	0·81	0·35
Fe_2O_3 in glass (%)	0·216	0·24	0·24	0·24

Trouble shooting glass oriented problems

In a flint glass in which Calumite slag was being used and therefore well refined, there was a sudden change such that the glass became consistently seedy. Checking the glass, it was found that the retained SO_3 was higher than normal, and also the proportion of ferric to total iron had increased. Obviously, the glass had become more oxidising. The weighing scales were all checked and none was found to be incorrect, but on checking the raw materials it was found that the limestone was not to specification and contained 2% gypsum. Therefore, as there were 500 kg limestone in the 2000 kg sand batch, it was possible to correct the seed problem by returning the redox to its normal level by the removal of half of the 20 kg of sulphate also present.

A second example is of an amber batch which was modified to become a Calumite slag batch with no sulphate as the carbon–sulphate batch had given variable colour and blister. To use the recommended level of Calumite slag, it was necessary to remove all the carbon from the batch; even then, the glass was darker than required so the Calumite slag content was reduced to bring the colour within the acceptance limits, but the blister problem returned. Examination indicated that the carbon content of the sand was varying, with the result that it was adding $\frac{1}{2}$–$4\frac{1}{2}$ kg of carbon per 2000 kg of sand to the batch, causing the redox number of the glass to fluctuate from −18 to −54. The higher carbon content caused sulphur to be retained in the glass in the reduced state, which later in the melting process became oxidised and visibly evident as blisters. It was arranged for the sand to be washed before delivery, thus removing some of the carbon so that the level, while still high, was more stable. This allowed the redox number of the batch to become less negative, the Calumite slag being increased to compensate. The ideal way to control colour with a no sulphate batch is to have about $\frac{1}{2}$ kg carbon in the batch, but in this example the sand was already contributing about $1\frac{1}{2}$ kg carbon and to prevent this from holding the sulphide sulphur in the glass and to keep the redox number at the optimum level for good colour, it was necessary to add some sulphate. This eliminated the blisters due to the late release of sulphide sulphur in the furnace and gave control of the colour. It allowed the Calumite slag content to return to the level recommended for good amber glass production.

Making colour changes

Changing from an oxidised glass, such as flint or green, to a reduced glass, such as amber, has in the past required the furnace to be drained, flushed, and filled. Changing from flint to green did not cause any major problems, but when changing from glasses of substantially different oxidation states, severe foaming was encountered. This is less so now that most flint glasses are less oxidised, following the introduction of Calumite slag. Previous work[5] which has since become the subject of a patent,[6] has shown that the use of the redox number concept has allowed the state of oxidation of the glass to be predicted from its batch composition, thus enabling controlled and predetermined changes to the redox state of the glass to be made.

An example of this approach may be found in a change from amber to green, whereby the amber is allowed to become more oxidised until it is at the limit of colour stability and quality acceptance; the glass is held at this state for a time until it is 'pre-conditioned' and is then moved through the critical sulphur solubility zone in a series of predetermined changes to its oxidation state, using the redox number concept to calculate the changes required. This produced minimal foaming.

It is claimed that production of off-colour unsaleable ware has been greatly reduced by using this method. Other benefits have been: the elimination of the need for large volumes of quenching water; less refractory wear—previously, draining the furnace also removed the protective viscous glassy reaction layer adjacent to the refractory surface, so that the fresh glass had a new refractory surface presented to it, without any protection; production machines can be run in, ready for the colour to become saleable whereas, before, this could not be done until the furnace had been refilled; if molybdenum electrodes are used there is always a danger of damage when a tank is empty due to exposure and oxidation which the above system eliminated.

Improved furnace efficiencies

It is often suggested that the use of carbon with sulphates is the best way of refining flint glass. The following example shows the effect of changing a flint batch to eliminate carbon and introduce Calumite slag, while retaining the redox state more or less constant. The batches used are given in Table 4 and it may appear surprising that they gave a slightly negative redox number, but this indicates the use of the principle of finding the optimum number for each melting unit. In this case the furnace was fired by natural gas with a more oxidising atmosphere. However, the results of the change to a Calumite slag batch with the same redox number and the same glass

Table 4. *Progressive changes in a batch, maintaining a redox number of −1·3*

Batch components	*Batch* *A*	*B*	*C*	*D*
Sand	2000	2000	2000	2000
Soda ash	667	670	673	676
Limestone	573	543	514	485
Feldspar	300	275	251	227
Calumite slag	0	33	65	87
Barytes	16	16	16	16
Carbon (65%)	1·77	1·10	0·45	—
Redox number	−1·3	−1·3	−1·3	−1·3

colour were as shown in Figure 3: a fuel saving of approximately 10%; a furnace temperature reduction of approximately 30 degC; a reduction in seed count from an average of 80 to an average of 30; with all the above benefits it was also possible to increase throughput from 160 to 185 tonnes per day.

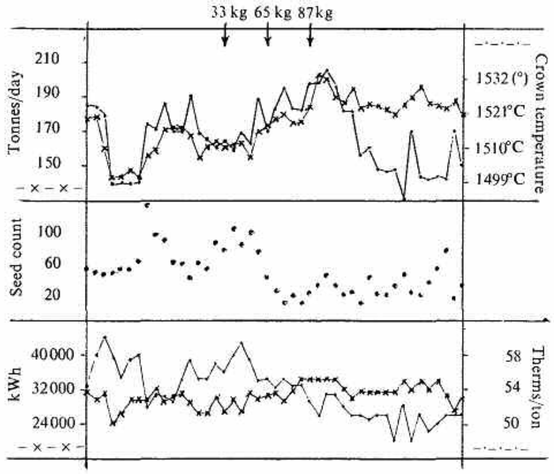

Figure 3. *Effect of additions of Calumite slag*

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