Creating markets for recycled resources

R&D Report: Glass

Feasibility Study for the Reduction of Colour within the Glass Furnace

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Executive Summary

Two of the greatest issues facing closed-loop recycling of container glass in the UK at present are the colour imbalance of glass packaging consumed versus that which is manufactured and whether to collect containers mixed or colour separated.

Container glass recycling is driven by the Packaging Waste Regulations that sets recycling targets for all packaging materials. The target for 2008 is 60% of all glass packaging will have to be recycled. This represents a doubling in the recycling rate and will generate 1.32 million tonnes of recycled glass (cullet). At this level of recycling the glass container manufacturing sector could consume 919,000 tonnes of recycled glass but there would be a surplus of some 400,000 tonnes of green glass. The reason for this is the imbalance between the colour mix of recycled glass (cullet) and the colours produced by the UK container industry; about half of the recycled glass is green but the UK glass container manufacturing sector is biased towards the production of clear (flint) glass.

The problems of surplus green or collecting mixed colour could be resolved if the cullet colour can be rendered immaterial through cost effective neutralisation of the colour of the glass in the furnace.

The purpose of this project was to undertake a programme of research into the feasibility of neutralising glass colour in the furnace. The work comprised a worldwide literature survey, with a series of laboratory-scale trials to assess the viability of a more comprehensive future project in this area.

Project Team

The work was carried out jointly between Glass Technology Services and the University of Sheffield, Engineering Materials Department under the guidance of Dr John Parker. In addition, Dr Parker's undergraduates undertook a series of experiments to investigate colour reduction as part of their practical studies.

The project received support from The Waste and Resources Action Programme (WRAP). The project was run by a steering committee comprising from interested partners, including:

- WRAP – Funding body;
- Glass Technology Services Ltd (GTS);
- University of Sheffield, Engineering Materials Department;
- Rexam Glass (supply of information and materials);
- Additional representation from the UK Container Manufacturers.

Glass Colouring Mechanism

Commercial green container glass is coloured by additions of approximately 0.25 wt% chromium oxide (Cr_2O_3) and 0.35 wt% iron oxide (Fe_2O_3) and amber (brown) is essentially coloured by 0.5wt% iron oxide in a reduced state. Both chromium and iron oxide are relatively strong colouring oxides in container glass. Therefore, flint (clear) container glass must only have trace additions of chromium and iron to avoid visible colour; a slight green/yellow colour is generally masked by adding a decolouriser. However, the addition of decolouriser can result in loss of light transmission and result in a grey appearance in the flint glass. Commercial flint container glass generally has no more than 0.5wt% of green glass added as cullet.

Techniques Investigated

This study reviewed reported methods for reducing the colour of container glass and other possible approaches from other industries such as metal extraction. Throughout this work the technicalities of the possible routes were reviewed and appropriate observations made. The practicalities and economics of the possible routes were not fully investigated, however, where appropriate comments have been made on the possible adoption of the investigated techniques. The following methods were investigated:

Dilution, decolourising & colour balance

The use of coloured glass in flint melts is nothing new; in fact the level of coloured glass used in flint glass was once relatively high and glass makers were able to compensate with decolouriser additions. However, the amount of coloured glass in flint melts has reduced over recent years due to improvement in cullet processing with coloured glass removal equipment. Therefore, glass makers tend not to have the need to regularly modify the melt by using decolourising additions.

From the literature and experimental work undertaken there appears to be scope for investigating the use of a controlled addition of green and/or amber in flint melts. Currently the addition of green in flint is up to 0.5% in the final glass (<6000 tonnes/annum). At these levels the current decolourising addition is adequate. However, with further investigation it should be possible to increase the level of green in flint. Based on current flint container glass production of approximately 1,200,000 tonnes/annum using a 40% cullet addition of which 3% is green cullet, then there could be a possibility of using 14,000 tonnes/annum. This could be further increased with higher cullet additions with slightly higher green cullet levels. With amber in flint it should be possible to increase further the addition, as amber tends to pull the colour away from green towards yellow/red.

Amber glass is far more tolerant of green cullet; up to 30% green cullet can be used in amber glass. Currently, amber glass production is only using approximately 20% cullet, this is primarily due to the lack of supply of amber cullet. Therefore, if amber glass production was capable using 30% green cullet this could equate to approximately 75,000 tonnes/annum. However, the main consideration and limitation is the redox* of the melt that needs to be controlled and monitored during melting.

This route has the potential to absorb controlled levels of coloured glass, but further industrial research is required to fully understand the limitations. One important consideration that was not investigated as part of this project is the consumer perception of slightly coloured glass containers. Market research needs to be undertaken to fully understand the impact of slightly coloured and/or loss of light transmission on the perception of glass containers as a suitable food or beverage container. It is known that flint containers produced in other European countries can be significantly coloured.

Crystallisation and phase separation

During commercial glass melting it is known that under certain conditions the glass can start to crystallise to form phases that are richer in certain oxides. Within the scope of this project it was not possible to practically investigate this route. However, the literature indicates that this route has the potential to produce relatively pure (>99%) compounds such as silica. However, there was only limited work undertaken and further research needs to be conducted.

Reductive melting

With the use of a reductive melting method such as that used in metal extraction, it may be possible to reduce the iron and chromium oxide to the metal form. Practical work investigated the use of silicon metal to form an alloy that would contain Cr & Fe. However, it was found that the Cr & Fe in the metal inclusion was only from the surrounding glass due to the slow diffusion rate of Cr & Fe through the molten glass. Therefore, the overall Cr & Fe from the bulk glass was only slightly reduced. Also, the colour of the glass (green) was not reduced, in fact, due to the reducing conditions it appeared slightly darker in colour.

This route required the formation of metallic silicon, which is an inclusion that can cause catastrophic failure if embodied in the final glass container. Therefore, this route would not be appropriate as a method used in the glass melting furnace.

Electrochemistry

Electrochemistry is used in the extraction of metals from solutions, and considering molten glass as a liquid the mechanism of electrochemical extraction was investigated. Within the scope of the project it was not

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[*] Term used to describe the balance between the reducing and oxidising species in a glass melt, positive redox is an oxidised state, whilst negative is a reduced state.

possible to undertaken practical experiments for this route. The extraction of metal ions from molten glass is theoretically possible. However, there are practical limitations such as suitable electrode materials and high temperature to reduce glass viscosity. This route has the potential to reduce the level of colorant ions. However, there was only limited work undertaken and further research needs to be conducted.

Wet chemical extraction

It is possible to extract the pure silica from glass by an alkali fusion route, the experiments undertaken were very promising, producing relatively pure silica sand that could be used in glass making or other applications requiring finely ground high purity silica.

Another technique investigated was acid washing of finely ground coloured glass to remove the Cr & Fe from the surface of the glass particle. However, this route was found not to produce a suitable feedstock material for glass making as there were still considerable levels of Cr & Fe in the bulk of the glass particle.

The practicalities and economics of the alkali fusion route need to be investigated further before recommending it as a possible solution for removing Cr & Fe from green and amber cullet.

Alternative colouring system - Irradiation

It is known that the exposure of container glass to x-ray energy can result in a brown coloured glass. Practical work indicated that it is possible to induce colour which was predominantly amber, however, it is known from previous work that the colour can quickly fade. Therefore, silver oxide was used to stabilise the colour, however, due to the short timeframe of this project it was not possible to determine how long the colour will be stable.

This route has the potential for manufacturers to melt only flint glass that is then coloured by irradiation. This would obviously have many implications on glass manufacturing and recycling. In addition, it would allow the manufacturer to apply colour patterns to the glass container by masking certain areas. Further research needs to be conducted to validate this route as a commercially viable approach.

Recommendations for Further Work

The literature survey and practical work indicated that the following, in order of priority, were worthy of further investigation:

1) *Dilution, decolourising & colour balance* - Scale up project initially undertaking large scale laboratory melts then moving to industrial trials. This would work as an industrial club project. The project should include the development of a computer model that would allow furnace managers to input the cullet level and colour composition and then determine decolouriser level. This route has the potential in the short term to increase recycled glass back into primary glass melting.

2) *Irradiation* - In-depth research and development project to fully investigate the technique of colouring glass by irradiation, with a commercial and marketing study on the viability of colouring flint glass by irradiation.

3) *Crystallisation and Phase Separation* - Research and development project to investigate the technique of crystallising desired phases out of coloured container glass.

4) *Alkali Fusion (Wet chemical extraction)* - Research and development project to fully investigate the technique of producing pure silica, including the identification of possible markets for the product.

The other routes identified and reviewed as part of this work were considered not worthy of further investigation in the short term.

Contents

1 Introduction

Two of the greatest issues facing closed-loop recycling of glass in the UK at present are the colour imbalance of glass packaging consumed versus that which is manufactured and whether to collect containers mixed or colour separated. Both these problems could be resolved if the cullet colour can be rendered immaterial through cost effective neutralisation of the colour of the glass in the furnace.

Glass is a major packaging material and it is estimated that around 2.2 million tonnes of waste glass bottles and jars enter the waste stream every year. In 2002, approximately 750,000 tonnes of this waste glass was recycled, representing a recycling rate of 34% which is quite poor compared to many other European countries that achieve recycling rates of over 80%. Container glass recycling is driven by the Packaging Waste Regulations that sets recycling targets for all packaging materials. The future target for glass recycling in 2008 will be 60%, which is equivalent to 1,320,000 tonnes per annum (based on currently glass waste arisings) of waste glass to be recycled. At this level of recycling the glass container manufacturing sector could consume 919,000 tonnes[1] of recycled glass based on current cullet specifications, but there would be a surplus of some 400,000 tonnes of green glass. However, with improvements in cullet processing the glass industry could increase cullet consumption up towards 1,100,000 tonnes due to enhanced cullet quality. The reason for the imbalance between the colour mix of recycled glass (cullet) and the colours produced by the UK container industry; about half of the recycled glass is green but the UK glass container manufacturing sector is biased towards the production of clear (flint) glass.

The purpose of this project was to undertake a programme of research into the feasibility of neutralising glass colour in the furnace. The work comprised of a worldwide literature survey, with a series of laboratory-scale trials to assess the viability of a more comprehensive future project in this area.

The work was carried out jointly between Glass Technology Services and the University of Sheffield, Engineering Materials Department under the guidance of Dr John Parker. In addition, Dr Parker's undergraduates undertook a series of experiments to investigate colour reduction as part of their practical studies.

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[1] WRAP Research Report 'Recycled Glass Market Study & Standards Review – 2003 Update', 2003.

2 Glass Colour Mechanisms

Glass can be coloured by several different mechanisms. These include dissolved ions (predominantly transition metal and rare earth ions), metal-anion complexes such as the iron-sulphide amber (brown in colour), precipitated particles (e.g. the ruby colours produced by copper, gold or cadmium compounds), and finally combinations of different redox[2] species at relatively high concentrations. The first two form the basis of most coloured containers.

The most commonly used transition metals are Fe, Cr, Co and Ni. Rare Earths are generally more costly and are rarely used for bulk glass production. The precise colour introduced depends on the oxidation state of the ion and this in turn can be influenced by the batch composition and melting conditions. It also depends on the site adopted by the ion in the glass structure; this changes relatively little without major compositional adjustments but is an aspect of the complexity of typical absorption spectra. Normally iron will give a dull greenish colour to the glass, chromium a brighter green, cobalt blue and nickel a brown/grey shade. The intensity of the colour depends primarily on the concentration of the dopant species. Removal of the colour from such glasses will normally require removal of the colorant ions since changes caused by redox or structural state are limited and difficult to achieve.

The concentrations required are relatively low; for example a chromium green glass may contain just 0.25wt% chromic oxide as colorant. If other species are present the light absorption spectra generally are additive unless both species have more than one oxidation state – in that case one species may oxidise the other. This is exemplified by chromium which can exist in a 3+ and 6+ state. The latter state is generally regarded as unacceptable in a container since the free ion has been shown to be carcinogenic. In the absence of other species some Cr^{6+} will often form with typical melting conditions. If iron is also present in significant proportions Cr^{6+} tends to oxidise any ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}), and is itself reduced to the Cr^{3+} state, the green chromophore. Most green glasses coloured by Cr therefore also contain significant levels of iron, and the iron itself tends to reinforce the green colour.

An iron-carbon amber derives its colour from a complex unit consisting of a ferric iron, a reduced sulphide ion and three oxygens. The colour is destroyed by the absence of either iron or sulphur. Further since one of these species is in an oxidised state and the other in a reduced state, the range of glass redox states over which the colour occurs is limited. The colour seen varies as the concentration of both iron and sulphide. As a result dilution is more effective than for transition metals since halving the concentration can reduce to a quarter the concentration of complexes present. This hypothesis, however, is incorrect if further sulphide ions are introduced as part of the refining process.

Colours such as dead leaf (feuille morte), utilise a combination of chromium green and iron amber, providing a product with a distinctive colour but also one where the amber chromophore stops UV transmission; chromium on its own has only a limited effectiveness as a UV filter unless high concentrations of the 6+ state are present. Others colours used are mostly shades of the above colours where the colorant species is at a lower concentration; there are for example sky blues based on low cobalt concentrations and pale greens based on chromium at levels of approximately one tenth of those for standard green bottles.

In clear glass even low concentrations of the transition metals cause a noticeable change of colour and this is particularly observable in the base of the container, because of the greater glass thickness there. Iron is the most common impurity and must be obtained at low levels, the limits typically being set lower for high value contents. Iron, in its normal concentrations and oxidation states, produces a green hue although oxidation makes this a pale yellow and reduction gives a bluish hue (or amber in the presence of sulphate as a refining agent). In general a more oxidised state is preferred and the colour seen is balanced by adding low concentrations of cobalt (blue) and selenium (pink), these are termed as decolourisers. The resulting neutral tint is less noticeable than the iron green.

The persistence of many of these colorants makes recycling more difficult in general since colour separation is required. Low levels of impurities are present in the natural raw materials and so perfect colour separation

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[2] Term used to describe the balance between the reducing and oxidising species in a glass melt, positive redox is an oxidised state, whilst negative is a reduced state.

is not necessary but typically more than 0.5 wt% of green glass cullet in a clear (flint) glass will be just noticeable. Similar limitations apply to cobalt blue glass although amber is a less serious problem because melting under oxidising conditions can bleach the colour by destroying the sulphide species in the glass, and reducing the overall iron concentration.

Other colours are somewhat more tolerant of impurities but limitations still apply. The introduction of other colours into the waste stream will in the long term also yield a long term deterioration in the composition as impurities build up over time.

This project is designed to address many of these issues. There is no simple mechanism for removing low concentrations of chromium, cobalt or iron from the glass (e.g. by the use of temperature) but more complex chemical methods for purification are available; this project considers a range of possible solutions and their viability.

3 Literature Review

This chapter includes a brief review of the published research on the reduction of colour in various glass systems. Details of practical work under by GTS and University of Sheffield are included later in the report.

From the initial project meeting the following were agreed as possible routes worthy of further investigation:

- Dilution, decolourising & colour balance;
- Crystallisation and phase separation;
- Reductive melting;
- Electrochemistry;
- Wet chemical extraction;
- Alternative colouring system - Irradiation.

3.1 Dilution, Decolourising & Colour Balance

The principle of decolourisation has long been used to mask the effects of colorant impurities in glass manufacturing. Notable amongst these impurities are chromium, iron and manganese. In the case of mixed cullet, this is exacerbated by the presence of deliberately-added chromium and iron from green glass, iron from amber glass and other colorants such as cobalt from blue glass.

Complementary colours known as decolourisers are used to mask the colours of these impurities[3], such that the resulting colour is grey and hence tricks the eye into believing there is no colour. This only works up to a certain level, beyond which the loss of light transmission is noticeable.

Melting of mixed cullet is expected to give a colour too strong to mask by complementary colours alone. It is likely that some form of dilution in colourless cullet, plus appropriate decolourisation, could allow some level of mixed cullet to be melted into flint (clear in colour) cullet without compromising colour requirements. The levels and types of these variables must yet be determined, and will be investigated further in the melting trials.

Decolourisation of mixed cullet, which would be expected to form a green colour upon remelting, using complementary colours, would require the addition of elements colouring the glass red. This is severely limiting, as few methods of colouring glass red exist. The main method is ruby, which entails formation of small metallic particles, usually of copper or gold, upon heat treatment of glass.

The University of Sheffield is currently developing a predictive computer model that could be used to predict the glass colour based on the composition including the additions of cullet and trace compounds. The work is different from other previous studies in that numerous light transmission spectra will be studied and any correlation between light transmission and composition will be determined. This study is investigating glass compositions used for optical filter glasses; however, the methodology of the study could be further developed to include container glass compositions. The current study is in its early stages and it is planned to conclude in 2006.

3.1.1 Decolourising

Glass is decolourised by two methods namely chemical and physical[4]. Chemical decolourising is usually taken to mean oxidising of Fe to Fe^{3+} state from Fe^{2+}. Iron is present in glass in two oxidation states, Fe^{2+} and Fe^{3+}, both of which give rise to different optical absorptions, and hence the relative levels of Fe^{2+} and Fe^{3+} ions will affect the colour of the glass in addition to the overall Fe content.

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[3] M. Muhlbauer, Decolorizing crystal glass, *Bull. Amer. Ceram. Soc.* Vol. 74, No. 5, 1995, p.70.

[4] P.J. Doyle, Decolourising glass, British Glass Industrial Research Association, Literature Review No 12, 1981.

Iron in its reduced form, Fe^{2+}, gives glass a strong blue colour. This is due to a strong, broad absorption centred in the near-IR at about 1050nm, which extends to lower wavelengths in the visible region. Other weak absorptions also occur in the near-UV, however these are masked by Fe^{3+} absorptions. Oxidised iron, Fe^{3+}, gives rise to several narrow absorptions in the near-UV and blue wavelengths, causing a yellow-green colour. These absorptions are weaker than the comparative Fe^{2+} absorptions, hence the minimisation of colour requires the majority of iron in glass to be present in its Fe^{3+} form. Generally the iron redox ratio in container glass is approximately 20% Fe^{2+} and 80% Fe^{3+}.

Physical decolourising depends on colouring the glass to cancel out the colour imparted by the iron and other impurities. The commonly used decolourisers in flint glasses[5] are selenium, cobalt, manganese, nickel and rare earth compounds such as neodymium and erbium. The subject of decolourising glass is complicated by the various base glass compositions used in glass manufacture and there are a diverse range of approaches to decolourising. There are numerous publications that discuss the theory and practical approaches on glass decolourising.

When greater amounts of some decolourisers or when improper decolourising agents are used, the resulting glass may be too dark or sensitive to daylight (exhibiting solarisation).

Selenium and cobalt are probably the most widely used decolourants for flint container glass. The selenium is added as elementary selenium (Se) between 0.001 & 0.005% and cobalt added as cobalt oxide (CoO) between 0.0001 & 0.0005%. Selenium introduces a pink colour that partially masks the green from the Fe^{3+}. Müller-Simon & Kircher[6] reported that 12% of the selenium was retained in the glass, with most evaporating from the batch pile as it enters the furnace and being lost in the waste gas from the furnace. It is also reported[7] that of the retained selenium only 10 to 20% is an effective decolouriser, due to the oxidation state of the selenium as shown Table 1. Selenium is a relatively expensive batch material and is classified as a toxic material. Considering that more selenium would be required in the case of green cullet in flint glass production, this would have cost and environmental issues. There is the possibility of reducing elementary selenium usage by using selenium containing compounds such as zinc selenite[8] ($ZnSeO_3$), however, this would require further investigation as elementary selenium is the commonly used form of selenium. Elementary selenium is volatile at temperature above 400°C, whilst zinc selenite is thermally stable up to 850°C. Cobalt oxide shifts the colour towards a blue colour and is a relatively strong colorant. Cobalt oxide in combination with selenium will shift the perceived colour towards neutral (white).

← reduced		neutral	oxidised →	
Se^{2-} Colourless	$Se^{2-} + Fe^{3+}$ Pink to amber	Se^{0} Pink	Se^{4+} Colourless	Se^{6+} Colourless

Table 1 Oxidation states of selenium observed in container glass[7].

Honeyball[9] discussed the optical properties of glasses containing iron and chromium in great depth. Included in his studies were the effects of redox on optical properties of such glasses. In addition, Weyl[10] and Volf[11] both discussed these topics in their well-known works on glass.

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[5] D. K. Hill, The decolourising of soda-lime-silica glasses, *BGIRA Information Circular* No. 12, 1956.

[6] H. Müller-Simon & U. Kircher, Selenium flow in the meting of flint glass containers, Glastech. Ber., Vol. 69, No. 4, 1996, p. 107.

[7] H. Müller-Simon, J. Bauer & P. Baumann, Redox behaviour of selenium in industrial soda-lime-silica glasses, Glastech. Ber., Vol. 74, No. 10, 2001, p. 283.

[8] C. Merivale, Use of zinc selenite in glass manufacture, *Ceram. Eng. Sci. Proc.*,Vol. 17, No. 2, 1996, p71.

[9] W. A. Honeyball, Spectroscopy and Oxidation-Reduction Behaviour of Iron and Chromium in Soda Lime Silica Glasses, PhD Thesis, University of Sheffield, 1973.

[10] W. A. Weyl, Coloured Glasses, Society of Glass Technology, 1959.

[11] M. B. Volf, Chemical Approach to Glass, Elsevier, 1984.

Chromium occurs in container-type glass as Cr^{3+} or Cr^{6+}; however the $^{6+}$ form of chromium is highly toxic and legislation exists to limit the Cr^{6+} content of glass to parts-per-million (ppm) levels. Essentially, therefore, melting conditions must be controlled so that chromium is present in container glass only as Cr^{3+}. For example sodium sulphate[12] will shift the equilibrium towards the formation of hexavalent chromium (Cr^{6+}), however, Fe stabilises the trivalent (Cr^{3+}) and hinders the conversion of Cr^{3+} to Cr^{6+}. Therefore, Cr^{6+} is generally excluded (only trace amounts) from commercial container glass by controlled iron content and oxidizing furnace conditions. The Cr state reaction is dependent on many parameters and it is outside the scope of this study. The Packaging Waste Regulations limit the amount of lead, cadmium, mercury & hexavalent chromium allowed in container glass to 200 ppm. This limit is temporary following an EC derogation[13] on the limits set in 2001. However, this limit might be reduced to 100 ppm by 2006.

The ligand coordination of these colorant ions in glass can also strongly affect the colours they bestow, but various studies have shown that very strong variations in glass compositions, e.g. switching to phosphate-based glasses, would be required to affect significant changes in colouration. This is not possible in container glass, so coordination effects can largely be assumed to be constant. Small changes in coordination may occur with large redox changes, however these would only have a small influence on colour when compared with the effects of redox itself.

Dupont et al[14,15] patented a grey colour in soda-lime glass, using a combination of Fe_2O_3 (0.5-0.9%), Co (0.012 – 0.025%), Se (0.0025 – 0.01%) and Cr_2O_3 (0.005-0.02%). This glass was considered to be especially suited to sun-roofs in cars. Foguenne & Dupont[16] developed a grey-green glass with 0.9-1.8% Fe_2O_3, 0.001 – 0.01% CoO, 0.01 – 0.024% Cr_2O_3 and 0 – 0.2% V_2O_5 with 0.0003 – 0.0009% Se. This suggests that careful development can lead to a grey glass with high colorant content and that adding significant levels of coloured cullet to flint glass melts may be feasible if appropriate decolourisers are also used.

Another alternative could be to introduce an intermediate step in which the coloured cullet is turned into a grey glass with appropriate additions of colorants. This grey glass could then be introduced into the flint glass stream at a higher concentration. Whether this would require a new melting step or whether it could all be done in a one-step process cannot be fully ascertained in a desk study. However, evidence from the production of grey automotive glasses suggests this may be possible in one step. This successive dilution approach would only provide gains however if the intermediate material itself had applications so that some of the colorants were removed from the waste stream.

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[12] Ü. Güldal & C. Apak, A study on Cr^{3+}/Cr^{6+} equilibria in industrial emerald green glasses, *J. Non-Cryst. Solids*, Vol. 38, 1980, p. 251.

[13] Commission Decision, Establishing the conditions for a derogation for glass packaging in relation to the heavy metal concentration levels established in Directive 94/62/EC on packaging and packaging waste, 19th February 2001.

[14] C. Dupont & D. D'Hont, U.S.Patent No. 5,728,471, Glaverbel, March 17, 1998.

[15] C. Dupont & D. D'Hont, U.S.Patent No. 5,877,103, Glaverbel, March 2, 1999.

[16] M. Foguenne & C. Dupont, U.S.Patent No. 6,335,299, Glaverbel, January 1, 2002.

Typical colorant levels in the three main types of cullet are shown below in Table 2.

	Fe_2O_3 / %	Cr_2O_3 / %	SO_3 / %
Flint	0.07	0.002	0.21
Green	0.36	0.24	0.07
Amber	0.42	0.02	0.07

Table 2 **Colorant levels in main cullet colours.**

Clearly iron and chromium levels and redox are greatly different in the three glass types. A matrix was constructed to estimate the expected iron, chromium and sulphate levels in flint glass doped with varying levels of green and amber cullet. The results are shown below in Table 3.

	Fe_2O_3 / %	Cr_2O_3 / %	SO_3 / %
Flint Glass	0.0700	0.00200	0.2100
+1% Green	0.0729	0.00438	0.2086
+2% Green	0.0758	0.00676	0.2072
+5% Green	0.0845	0.01390	0.2030
+10% Green	0.0990	0.02580	0.1960
+1% Amber	0.0735	0.00218	0.2086
+2% Amber	0.0770	0.00236	0.2072
+5% Amber	0.0875	0.0029	0.2030
+10% Amber	0.1050	0.0038	0.1960

Table 3 **Estimation of contamination levels with varying cullet addition.**

Clearly the addition of 10% green cullet will seriously affect the colour of the final glass, increasing the chromium content by over 10 times. Even the addition of 1% green cullet doubles the chromium content of flint glass. On this basis it is expected that only substantially less than 10% green glass in flint would be acceptable, and certainly under 5% to stand a good chance of being effectively decolourised.

It is reported[17] that sometimes green cullet is purposely added to amber to deliberately induce a red tint. The addition of green cullet to amber melts is reported[18] to reduce light transmission at 550nm by approximately 0.15% per every percent addition above 10%. It would be expected that amber cullet added to a flint melt would also reduce the light transmission, however, there is no reported data of the possible transmission reduction. There are many reports in the public domain on the use of cullet in glass manufacture. However, there is little information on the colour composition of the cullet, which gives any indication of the colour mixes that have been successfully trialled.

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[17] D. Myers & R. Hulme, Optimising batch formulation and furnace operation, Glass Prod. Tech. Inter.,1995, p. 31.

[18] S.M. Weiser, The effect of amber cullet additions on amber glass transmission, *Ceram. Eng. Sci. Proc.*, Vol. 8, No. 3-4, 1987, p. 200.

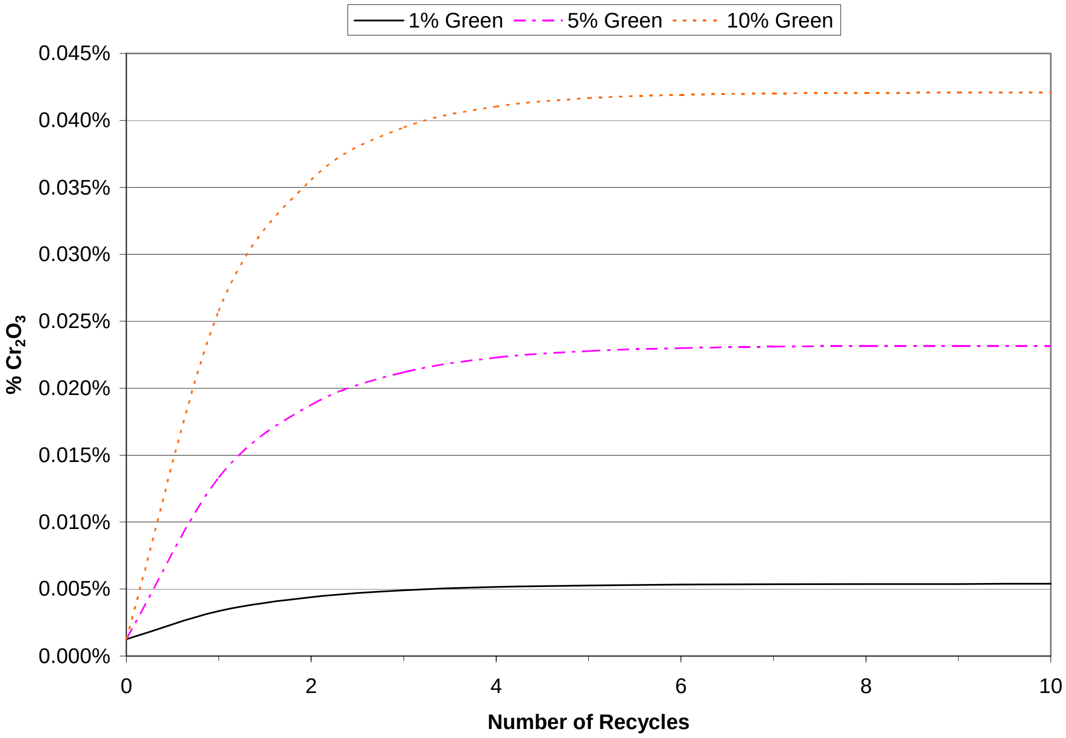

Figure 1 **The effect on Cr_2O_3 with continual recycling of green glass in flint glass melting. Based on 50% cullet of which the above are percentages of the total glass melted.**

3.1.2 Dilution

In addition to the decolouriser approach there is also the possibility of adding different coloured glass to a melt at levels that have no detriment to the product. However with continual recycling of more green in flint glass there will be an accumulation of Cr_2O_3 in the glass. The rate of increase will fall off after approximately 5 recycles, as shown in Figure 1 but a 5% addition of green in flint cullet would have seriously affected the colour of flint glass by that stage. The long-term accumulation effect must be considered in any attempt to add green to flint glass and decolourise.

The possible addition into flint glass of amber glass is a different case to green. If redox barriers and possible issues with foaming and stones can be avoided or overcome, it is potentially feasible that higher levels of amber cullet might be added due to the absence of chromium in amber cullet.

Mixed cullet contains essentially a mixture of green and amber cullet, with some level of flint and low levels of other colours. It is likely, therefore, that mixed cullet would be more forgiving than green glass in terms of the acceptable addition levels to allow effective decolourising, but less versatile than amber cullet. Based on the calculations shown in Table 3, it is hoped that additions of several percent of amber cullet and a few percent of mixed cullet could be effectively decolourised in flint glass.

Skornyakov[19] made a study to establish correct levels of decolouriser in flint soda-lime silica glasses. In particular it was noted that with large quantities of Fe_2O_3 and Cr_2O_3 in the glass, the cobalt should be increased. Other workers[20] noted that selenium and cobalt are widely used for decolourising purposes in container glass.

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[19] M.M. Skornyakov, Decolourising glass, *Steklo I Keramika*, Vol. 16, No. 12, 1959, p. 29.

[20] Decolourisation of glass, J. Chem. Educ., Vol. 42, 1965, p. 160.

Moutsatsou et al[21] discussed the introduction of up to 50% coloured cullet into amber glass, and found that at 10% and 30% green cullet additions, the amber colour could be adjusted through redox changes brought about by carbon additions to the batch of between 0.25 & 0.3% carbon for 30% green cullet addition. At 50% green cullet addition, however, other problems occurred concerning bubbles as well as colour, indicating the reasonable maximum for green cullet additions was 30%. This is still a very large proportion of the glass and points to many different possibilities regarding the use of mixed cullet in amber glass manufacture. Similarly, Mosch[22] discussed the addition of mixed cullet into amber glass. This was done by regulating the amounts of iron, carbon, sulphur and sulphur compounds into the mixture to give the required colour. In the preferred example of Mosch's patent, mixed cullet is mixed with a carbon-sulphur amber batch and therein treated with decolourising compositions, to produce carbon-sulphur amber glass which contains substantial amounts of colour converted mixed coloured cullet.

With the introduction of a different colour glass into a melt, there will be a need to know the redox state of the melt. A development group[23,24] run by TNO, Institute of Applied Physics has recognised the need for measuring the redox state at varying levels of cullet additions and has developed a glass redox measurement system. As part of the development the equipment and software was extensively tested and it is reported that the method was suitable for industrial application. If this equipment and method is robust enough for continual monitoring then this will have advantages in controlling the glass colour when using mixed colour and/or high cullet additions.

Beerkens[25] reported that the particle size of the cullet affected the redox of the melt around the cullet particle. Finer cullet particles will start to sinter together around 700°C, preventing the penetration of the oxygen from the furnace atmosphere, whilst the furnace atmosphere has an effect on the larger sized cullet, resulting in a glass of a lighter green compared to the finer cullet particles. This means that the effect of the furnace atmosphere on the colour due to redox reactions is a function of the cullet particle size. Therefore, as the cullet addition increases as more glass is recycled then the effect of cullet particle size will become a parameter that needs to be managed.

A well-known decolouriser for giving grey tints is nickel. Thorpe[26] discussed the use of NiO in works trials to decolourise glasses containing 0.033 to 0.061% Fe_2O_3. The NiO additions were about a factor of 15-20 lower than the Fe_2O_3 levels. Small additions of selenium and cobalt aided decolourisation of these glasses even further.

The addition of some level of green or amber glass into flint glass would also bring about changes to the glass redox. This in turn can impact upon colour and melting problems such as refining and reboil. Simpson & Myers[27], and DiBello[28] discussed the phenomenon of redox in detail, in particular its effect in container glass manufacture. In terms of this project, the situation is best summed up by Figure 2 from DiBello's paper. As the glass becomes more reduced, the total sulphur retained in the glass decreases linearly down to about 0.03% SO_3 retained, which corresponds to glasses with olive-green colour. Further reduction does not decrease the retained SO_3 further, but forces the glass to become amber. Therefore amber glasses can be returned to essentially flint glasses by re-melting under specific conditions. This therefore sets them apart from traditional green glass, which contains chromium and is therefore not covered by this model.

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[21] A.K.Moutsatsou et al, Study of the addition of coloured cullet in the production of amber glass, *Proc. Int. Symp. Recycling and Reuse of Glass Cullet*, Univ. Dundee, Scotland, March 2001, p.43

[22] A. Mosch, U.S.Patent No. 5,718,737, D., February 17, 1998.

[23] A.J. Faber, Redox control during industrial melting of cullet rich glass batches, *Glass Technol.*, 1997, Vol. 38, No. 6, p. 189.

[24] R. Beerkens et al, Measuring the redox state of cullet, *Glass*, October, 1997.

[25] R. Beerkens, Redox and sulphur reactions in glass melting process, Silikáty, 1999, Vol. 43, No. 3, p123.

[26] C. Thorpe, A works trial of the use of nickel oxide as a decolourising agent for certain container glasses, British Glass Industrial Research Association, Technical Note No. 2, 1956.

[27] W. Simpson & D.D. Myers, The redox number concept and its use by the glass technologist, *Glass Technol.*, 1978, Vol. 19, No. 4, p. 82.

[28] P. DiBello, Controlling the oxidation state of a glass as a means of optimising sulphate usage in melting and refining", *Glass Technol.*, 1989, Vol. 30, No. 5, p. 160.

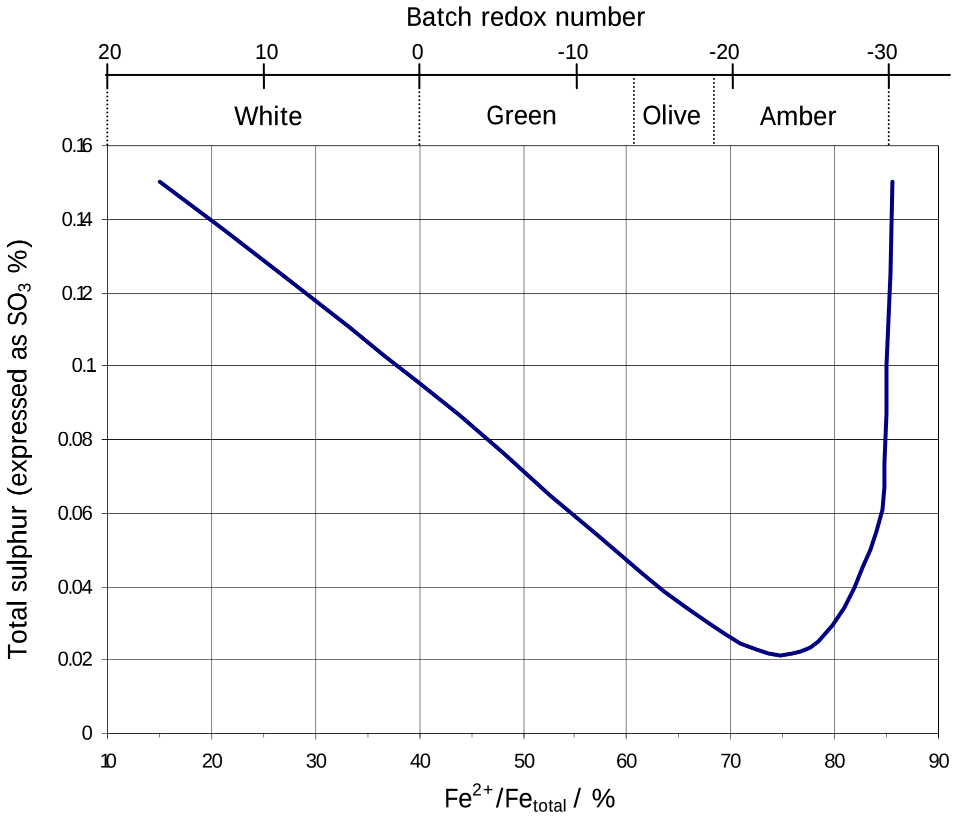

Figure 2 **The solubility of SO_3 in glass as a function of its redox state[28].**

It should therefore be possible, with the correct melting parameters, to take some level of amber glass cullet, and melt it into flint glass. As shown in Table 2, the iron content of amber glass can be 5 or 6 times that in flint glass, so again the limitation of how much it is possible to add and decolourise comes into play. It is likely that the addition of 10% amber cullet would not greatly affect the overall colour of flint glass, providing it can be adequately decolourised.

Payne & Marcondes[29] undertook a series of trials investigating the addition of high levels of amber cullet in amber melts. They found that cullet levels could be taken up to 70% with appropriate sulphate correction to the batch. They did not report the colour composition of the amber cullet, however, it is likely that the cullet would have been colour contaminated with flint and green cullet. Nix[30] undertook a study on the redox numbers for externally sourced cullet as shown in Table 4, this allows the calculation of the batch in relation to the cullet addition. This will allow redox control of the melt and in turn allow high levels of cullet additions.

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[29] D.A. Payne & J.A. Marcondes, Effects of cullet level on quality of amber glass bottle, *Glass Technol.*, 1994, Vol. 35, No. 5, p. 230.

[30] M. Nix & H. Williams, Calculation of the redox number of glass batches containing recycled cullet, *Glastech. Ber.*, 63K, 1990, p. 271.

Cullet Colour	Redox Number
Flint	+ 2
Emerald green	- 8
Amber	- 20 to -25

Table 4 Redox number for externally sourced cullet[30].

3.1.3 Specification

There is currently no formal standard for furnace-ready cullet used for the manufacture of container glass, However, a typical glass manufacturer cullet quality standard was published by WRAP[31], which is shown in Table 5. It can be seen that the level of green and amber in flint glass is relatively low <0.5%. It is reported[32] by some UK container manufacturers that green in flint above 1% will require high levels of decolouriser resulting in a lower transmission glass that will have a grey appearance. However, this statement will be investigated and qualified by experimental investigations later in the report.

Standard	Typical Limits	Typical Levels
Ferrous metals	<50 g/tonne	flint 20-40 g/tonne amber 20-35 g/tonne green 20-35 g/tonne
Non-ferrous metals	<20 g/tonne	<1 g/tonne
Ceramics and stones	<20 g/tonne	flint 20-40 g/tonne amber 20-35 g/tonne green 20-35 g/tonne
Organics	3,000 g/tonne	flint 1,000-1,500 g/tonne amber 1,000-1,800 g/tonne green 1,200-1,800 g/tonne
Moisture	shows no drainage	shows no drainage (<2%)
Particle size	<50 mm	<50 mm
Principal Colour	**Typical Limits**	**Typical Levels**
Flint	amber <2% green <2%	amber negligible green 0.5%
Amber	green <10% flint <12%	green 0-10% flint 2-8%
Green	amber <10% flint <12%	amber 0-10% flint 0-10%

Table 5 Typical glass manufacturer cullet quality specification[31].

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[31] Recycled Glass Market Study & Standards Review, WRAP, 2003.

[32] Private communication.

The specification shown in Table 5 is for cullet after processing, the degree of required processing is a function of the quality of the cullet at the processor gate, as received from the cullet collectors. Until recently, there was no specification for cullet, however, BSI have published a Publicly Available Specification[33] (PAS 101). This specification has four grades of cullet; the specification for Grade A cullet is as follows:

Flint	96% flint, 4% other colours
Amber	85% amber, 15% other colours (max. 10% green)
Green	70% green, 30% other colours

These limits are relaxed somewhat in Grades B, with 6% contamination in flint, 30% in green and 15% in amber and grade C & D are classified as mixed colour glass. In addition, high contamination by blue glass is to be avoided so actual blue glass levels must be much lower than these maxima.

3.1.4 Summary - Dilution, Decolouring & Colour Balance

The route of adding green or amber cullet to flint glass and green cullet to amber glass with a balance of suitable decolourisers appears to have potential to increase mixed colour usage. To date there has been little pressure for using mixed colour glass, however, with new collection systems becoming more predominant such as commercial collections and higher UK recycling targets, this will probably mean that more mixed glass will be available for use in flint and amber glass production.

Flint glass melters routinely accept 0.5% green in flint cullet; with between 40 to 50% cullet addition this equates to approximately 0.25% of the finished flint glass containing green cullet. This amount of mixed colour is easily decolourised and if the amount of mixed cullet was increased then the decolouriser addition will need to be corrected, bearing in mind that some glass manufacturers tend to fix the decolouriser addition and vary the cullet addition to achieve the desired colour.

With amber glass it is reported that 30% green cullet additions are possible provided that the redox of the melt is controlled.

This possible route of using mixed colour cullet has potential; however, the actual levels of cullet and decolouriser need to be studied further to understand the limits without loss of light transmission.

3.2 Crystallisation and Phase Separation

The mechanism of crystallisation may prove to be a route for colour removal if preferential crystallisation of chromium-rich and iron-rich zones can be achieved. It may then be possible to separate the Cr-rich and Fe-rich zones from the regions depleted in these colorants, using for example standard magnetic separation systems, and to re-use the remaining material in flint glasses with minimal decolourisation.

Crystallisation of container-type glass is well-documented. Rawson[34], Kreidl[35] and Scholes[36] discussed many of the main issues surrounding crystallisation of glasses in the soda-lime-silica system. From this work it can be noted that most of today's container glass compositions fall into the devitrite ($Na_2O.3CaO.6SiO_2$) phase field. Rates of crystallisation are strongly influenced by the exact chemical composition of the glass, however within the particular phase field, all container glasses will form devitrite upon crystallisation. An initial study on segregation of chromium and iron into the primary phase has started at The University of Sheffield. Initial research has been undertaking crystallisation at a relatively low temperature, ≈700°C; at this stage

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[33] Recovered Container Glass – Specification for Quality and Guidance for Good Practice in collection, PAS101, BSI, 2003.

[34] H. Rawson, Inorganic Glass-Forming Systems, , Academic Press, New York, 1967.

[35] N. J. Kreidl ,Glass Science & Technology, vol. 1, Glass Forming Systems, Chapter 3, , Academic Press, 1983.

[36] S. R. Scholes, Modern Glass Practice, , Cahners Books, 1975.

the chromium appears to segregate into the liquid phase. However, the work is not advanced enough to report overall findings at this stage.

Mixed coloured cullet mainly contains a mixture of flint, amber and green glass. The primary colorants in these glasses are iron and chromium. The effects of chromium on crystallisation have been documented by several workers, who noted that it can have a strong influence on temperature and crystallisation rate.

Zhunina et al[37] discussed the addition of Cr_2O_3 to SiO_2 – Al_2O_3 – CaO – MgO – Fe_2O_3 glasses, and noted that upon adding 0.25 – 0.5% Cr_2O_3 the crystallisation behaviour was altered in terms of the crystalline phases produced and the rate of production.

Ashour & Shehata[38] discussed chromium aventurines, which can be made with chromium additions above or close to the solution limit. In alkali-alkaline earth silicate glasses, this limit occurs around 3 - 3.5% by weight of Cr_2O_3. Such contents are well above those present in container glass cullet, and as such the aventurine effect is unlikely to occur with any level of heat treatment. However the authors give useful information on the behaviour of these glasses: “When chromium oxide is added in amounts exceeding the supersaturation limit corresponding to ordinary melting temperature, the glass upon cooling from the molten state will yield a system of two immiscible supercooled liquids, the first is the base glass saturated with the metal oxide and the other is metal oxide rich but saturated with the other glass components. The metal oxide rich phase will tend, at high temperature, to disperse in the glassy phase in the form of submicroscopic droplets forming an emulsion.”

The implication of this statement is that at lower chromium levels, where supersaturation has not been achieved, the chromium is dispersed through the supercooled liquid and not in some separate phase.

Further discussion by these workers was as follows: “The first additions of chromium oxide dissolved in the glass as a true solute up to 0.5%......Further additions……gave rise to the formation of chromic oxide rich droplets during cooling.”

Transparent glass ceramics is a field where preferential crystallisation of colorant ions into certain phases could provide useful information. Tick et al[39], Beall[40] and Kang et al[41] all discussed this field in varying degrees of detail. The general principle was exemplified by the work of Wang & Ohkawi[42], who demonstrated that 20 nm cadmium lead fluoride crystals co-doped with erbium and ytterbium could be precipitated from aluminosilicate glasses, thereby yielding transparent oxyfluoride glass ceramics. Other workers have demonstrated similar effects using different dopants such as LaF_3.

If similar levels of control could be exerted over crystallisation from mixed colour glasses (major colorants iron and chromium), it may be possible to “load” a minor phase with colorant, thereby minimising the colorant levels in the bulk material.

Bahgat et al[43] discussed the reduction of iron-containing sodium borate glasses. They were able to melt a glass with 100% Fe^{2+} ions, by using $C_6H_{12}O_6.H_2O$ in the batch. However, these authors used Mössbauer spectroscopy to measure iron redox, and neglected certain critical considerations, which cast some doubt over the claim of 100% Fe^{2+}. Despite this it appears likely that the Fe^{2+} content of this glass was high. The authors stated that a ferrimagnetic phase precipitated in 5% Fe_2O_3 glasses i.e. preferential loading of the crystalline phase with iron occurred at the expense of the glassy phase.

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[37] L. A. Zhunina et al, Crystallisation of glasses of composition CaO – MgO – Al_2O_3 – SiO_2 in the presence of Cr_2O_3 with formation of a stable pyroxene phase, The Structure of Glass, vol. 3, Consultants Bureau, New York, 1964, p.192.

[38] G. M. Ashour & A. M. Shehata, Study of crystallisation of chromium oxide in glass (chrome aventurine), *Trans. Indian Ceram. Soc.*, Vol. 31, No. 6, 1972, p. 136.

[39] P. A. Tick et al, Transparent glass ceramics for 1300 nm amplifier applications, *J. Appl. Phys.*, vol. 78, No. 11, 1995, p. 6367

[40] G. H. Beall, Glass-ceramics for photonic applications, *Glastech. Ber.*, Vol. 73, C1, 2000, p. 37.

[41] U. Kang et al, Radiative properties of Nd-doped transparent glass-ceramics in the lithium aluminosilicate system, *J. Non-Cryst. Solids*, Vol. 278, 2000, p. 75.

[42] Y. Wang & J. Ohkawi, *J. Appl. Phys. Lett.*, Vol. 63, No. 24, 1993, p. 3268.

[43] A.A. Bahgat & H. El-Bahnasawy, Glass reduction: an laternativealternative approach to an old subject, *Glass Technol.*, 2001, Vol. 42, No. 2, p. 54.

A related approach has recently been proposed by a Japanese group[44]. They add significant amounts of B_2O_3 to cullet and melt to produce a borosilicate glass melt. The composition of this melt is designed so that it phase separates after appropriate heat treatment to give a silica rich matrix and a water soluble borate phases that contains most of the colorant ions as well as the added sodium and calcium. They optimised the composition, and melting and heat treatment conditions to give maximum extraction of Cr from the glass. The resulting leachant should allow the extraction of the colorants and also, after suitable chemical processing, the soda and boric oxide for recycling.

3.2.1 Summary – Crystallisation and Phase Separation

The formation of a crystalline phase that contains the primary colouring ions, Cr & Fe, is probably possible. However, it is likely that other glass forming constituents would also migrate to the crystalline phase, resulting in a glass or even another crystalline phase with a modified composition from the original glass container composition.

This route has the potential to produce relatively pure (>99%) compounds such as silica. However, there is only limited work undertaken and further research needs to be conducted.

3.3 Reductive Melting

Redox conditions of glasses do not only influence the colour of glass by shifting ionic states of colorants such as iron. If driven strongly enough, these redox states can be shifted to the reduced, metallic form. Hence, glasses melted under highly reducing conditions can form metallic inclusions from the reduction of the oxides in the glass to their metallic form. This is easily illustrated using an Ellingham diagram, as discussed by Paul[45] and shown below in Figure 3.

The Ellingham diagram clearly illustrates why, for example, one redox reaction is relatively easy to drive (e.g. $4Cu + O_2 = 2Cu_2O$), and why another requires extremely reducing conditions (e.g. $2Mg + O_2 = 2MgO$).

The use of carbon as a reducing agent clearly has certain limitations – its line occurs about halfway down the diagram. This means that it will readily reduce all reactions above it. For example Cu, Pb, Ni, Fe etc but not Cr, Mn, Si, Al, Li etc.

Interestingly, at glass melting temperatures of 1500°C, carbon will just drive the reduction of chromium from its $^{3+}$ state to the metallic state, in addition to the reduction of iron from $^{3+}$ to $^{2+}$ to the metallic state. This implies that it should be possible to form metallic iron and chromium, or at least metallic particles high in iron and chromium, at glass melting temperatures.

Reisch et al[46,47] discussed metallic silicon inclusions in container glasses from a number of different manufacturers. The glasses were prepared on a laboratory scale by melting with addition of metallic cuttings of aluminium and magnesium which in turn reduce the SiO_2 to metallic Si. This was done predominantly in flint glasses, but also in green and amber glasses. The metallic inclusions were found to be composed of silicon with a small amount of finely distributed iron-silicon alloying phases. In amber and green glasses, chromium, manganese and copper were additionally enriched as further main elements in these alloying phases. The light phase observed using reflected light in flint glass melts contained 40-50% Si, and 5-42% Fe, with additional levels of 0 – 2.2% Cr and 1-30% Mn.

The results for amber and green glass were less detailed, however this lighter alloyed phase was composed mainly of silicon, iron and chromium. The conclusions of Reisch et al were that metallic silicon spheres are formed in molten glass if metals such as aluminium enter the glass melt.

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[44] D Chen, H Masui, T Akai & T Yzawa, Decoloration of waste coloured glass through phase-separation and its mechanism, *J Australasian Ceram Soc.*, 2002, Vol. 38, No 12, 130-134.

[45] A. Paul, Chemistry of Glasses, Chapman & Hall, London, 1990.

[46] R. Reisch et al, Comparison of metallic silicon inclusions in industrial container glass and laboratory melts, *Glastech. Ber.*, Vol. 69, No. 10, 1996, p. 319.

[47] R. Reisch et al, Investigation of the dissolution of metallic silicon spheres in a container glass melt, *Glastech. Ber.*, Vol. 69, No. 11, 1996, p. 343.

An earlier paper by Reisch et al[48] noted the well-known problem that if metallic inclusions are present in molten glass, bottom corrosion is observed at higher temperatures. This consists of “downward drilling”, where essentially the reduced metal sinks to the bottom of the furnace due to its higher density, and corrodes the refractory. This can eventually result in failure of the furnace if sufficiently widespread. Therefore, the formation of metallic inclusions in a melting furnace must be avoided if at all possible.

The work of Reisch indicates that although preferential reduction of the colorants iron and chromium could be feasible in the molten state, unless a technologically and economically-feasible method of separating these metallic particles from the bulk glass can be found, this method has serious drawbacks.

The reduction of metals such as lead and bismuth from glass melts is a known problem in the melting of lead and bismuth containing glasses. Glass Technology Services[49] with DTI funding investigated methods for reducing lead and other metals from waste cathode ray tube (CRT) glass. It was found that the PbO content could be reduced by approximately 50% from initial PbO content of 5%. The limiting factor was the formation of metal spheres that were of a sufficient size (weight) to overcome viscosity of the glass and convection current, then settle at the bottom of the melt. The same limitation would apply to reducing Cr and Fe, also with one hundredth of the Cr and Fe content compared to the PbO in CRT glass, there would be a need to promote agglomeration and settling of the metallic particles.

Wischnat et al[50] discussed the formation of silicon in container glass melts. Aluminium was introduced as foil or pieces, reducing nearly the same amounts of silica in flint, amber or green glass. One point to be wary of is the fact that the alloys of aluminium which can end up in a glass furnace can often contain iron, chromium and manganese and unless caution is used this could be misinterpreted in terms of removal of iron and chromium from the glass. It was noted, however that more silicon spheres are found in oxidised flint glass than in green or amber glasses.

Weiser et al[51] discussed the metallic inclusions formed during glass production, with some emphasis on analysing them. Cross-sections of these particles showed the presence of different phases within the spheres. Analysis by EDX showed the presence of high levels of titanium, iron, manganese and copper. As with Wischnat et al, it may be possible these impurities came from the metallic aluminium, rather than some form of migration or reaction with the glass.

Clearly more investigation is required on a laboratory scale to establish the source of the high contaminant levels in the light phase of the silicon spheres. Using good quality cullet and pure reducing materials (aluminium metal or silicon for example) it should be possible to shed light on this issue.

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[48] R. Reisch et al, Thermal behaviour of metallic aluminium in a container glass melt, *Glastech. Ber.*, Vol. 69, No. 5, 1996, p. 123.

[49] ICER Report, New approach to cathode ray tube (crt) recycling, DTI report: GW-12.10-130, December 2003.

[50] V. Wischnat et al, Formation and oxidation of silicon in container glass melts, *Glastech. Ber.*, Vol. 66, No. 11, 1993, p.285.

[51] S. Weiser et al, How aluminium metal contamination affects container production, *Glass Industry*, June 1986, p. 14.

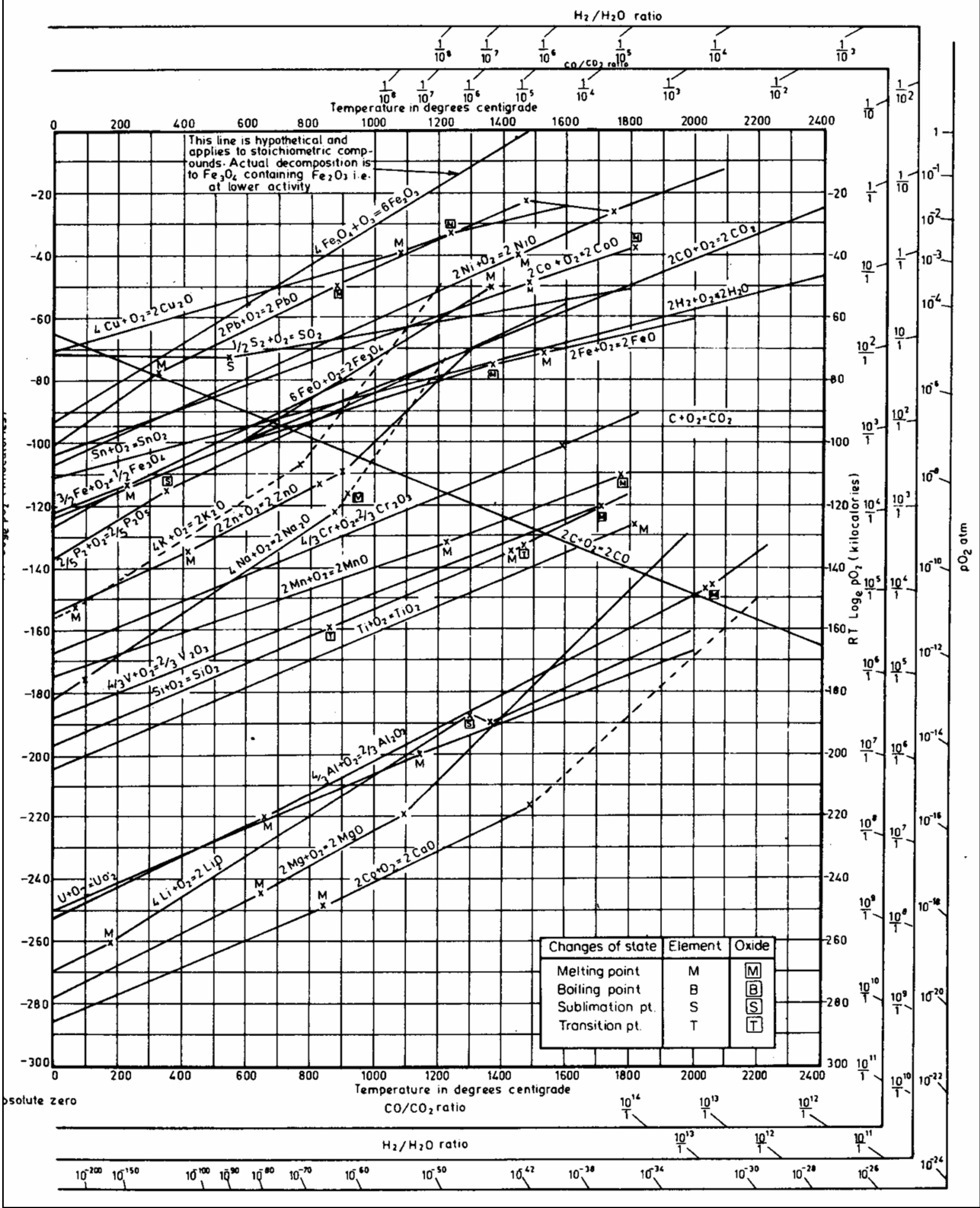

Figure 3 **Ellingham Diagram, element can reduce the oxide state to metallic form that is above it.**

3.3.1 Reduction with Electromagnetic Methods

Would it be possible to utilise the magnetic behaviour of iron in these particles to preferentially attract them, in the glass furnace, to one specific area, where:

a) they can be tapped out and removed and

b) the furnace refractories can be easily and cheaply replaced periodically?

Following on from this thought, the possibility of attracting or repelling these metallic inclusions could be carried out by applying a magnetic field to the molten glass. This could take advantage of the ferromagnetism of iron. Unfortunately, ferromagnetic behaviour collapses above the Curie Point[52], and the Curie Point of iron is 780°C. Hence in molten glass at 1500°C, iron would be well above its Curie Point, and ferromagnetic behaviour would be replaced by paramagnetic behaviour and then iron would behave as does chromium at all temperatures, i.e. paramagnetically. This means that a weak attraction will be formed upon application of an external magnetic field, instead of strong attraction as in ferromagnetic behaviour. Ferromagnetism also requires an appropriate crystal structure for the iron – the precise phase forming in an alloy mixture by reduction is currently not known.

Research carried out in the group of Warczok[53,54] in Chile has covered the effects of magnetic and electric fields upon molten slags and metallic inclusions therein. These have tended to focus on copper slags, but there is no reason to assume that the general principle would not be valid in different systems. Liquid slags in copper smelting contain dissolved copper as well as mechanically entrained inclusions of copper matte. Coalescence and sedimentation of inclusions plays a key role. Liquid matte inclusions give a metallic conductor within an ionic solution. A constant electric field applied through the melt induced migration of the matte droplets along the current lines.

Application of an additional magnetic field gave further effects, causing electromagnetic buoyancy in the metallic particles. Simulation of the behaviour of copper matte inclusions under crossed fields showed the trajectory of motion of the inclusions in the liquid slag were functions of the slag properties and the particle size.

Laboratory scale research showed in a simulated DC electric furnace with superimposed magnetic field, showed a significant acceleration in the rate of slag reduction and copper removal.

3.3.2 Diffusivity of Impurity Ions in Molten Glasses

Turkdogan[55] discussed the diffusivity of various ions in glasses at high temperature, based on the work of many other researchers. Work on Ni^{2+}, Co^{2+} and Fe^{2+} ions in calcium silicate glasses showed that all three diffusivities were about 2.6×10^{-5} cm^2 s^{-1}. The diffusivity of Ca^{2+} was about an order of magnitude lower.

In 67% Fe_2O_3 – 33% SiO_2 glasses the diffusivity of Fe^{2+} was 8.3×10^{-6} cm^2 s^{-1} at 1350°C, rising to 15×10^{-6} cm^2 s^{-1} at 1550°C. By comparison, the diffusivity of Na^+ in 67% SiO_2 – 33% Na_2O glasses was 62×10^{-6} cm^2 s^{-1} at 1500°C, and the diffusivity of Ca^{2+} in 63% SiO_2 - 37% CaO glasses at 1500°C was 1.7×10^{-6} cm^2 s^{-1}.

Von der Gonna & Russel[56] measured the diffusivities of Cr^{3+}, Cr^{6+} and Fe^{3+} ions in a $Na_2O.2SiO_2$ glass melt with varying temperature. At 1500°C the diffusivity of Fe^{3+} and Cr^{3+} ions is almost identical, at about 1.5×10^{-5} cm^2 s^{-1}.

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[52] A. Cottrell, An Introduction to Metallurgy, Edward Arnold Publishers, 1975.

[53] A. Warczok & G. Riveros, Effect of electric and magnetic fields on the metallic inclusions in a liquid slag, Yazawa International Symposium: Metallurgical and Materials Processing: Principles and Technologies; High Temperature Metal Production, v.2, 2003, p.417.

[54] V.Montenegro et al, Effect of Magnetic Field on the Rate of Slag Reduction in an Electric Furnace, Yazawa International Symposium: Metallurgical and Materials Processing: Principles and Technologies; High Temperature Metal Production, 2003.

[55] E. T. Turkdogan, Physicochemical properties of molten slags and glasses, The Metals Society, London, 1983.

[56] G. v. d. Gonna & C. Russel, Diffusivity of various polyvalent elements in a $Na_2O.2SiO_2$ glass melt, *J. Non-Cryst. Solids*, Vol. 261, 2000, 204.

It can be surmised that the diffusivity of transition metal ions such as chromium and iron is approximately an order of magnitude greater than Ca^{2+} but somewhat slower than Na^{+}. Since it is well known that sodium ions are highly mobile relative to the other normal glass constituents, these results indicate that transition metal ions are relatively mobile in silicate glasses.

However, the diffusion rates are still slow, of the order of 10^{-5} to 10^{-6} cm^2 s^{-1}. Typically this implies that a Cr ion will diffuse up to 3×10^{-3} cm after 1 sec and up to 0.18 cm after an hour. This may mean that reliance upon diffusion to cause significant agglomeration of chromium and iron into silicon balls could be insufficient.

3.3.3 Summary – Reductive Melting

The reduction of oxides to the metal form is possible in glass melts. However, in a typical container glass the major colouring ions, Cr & Fe, will account for less than 0.75 weight % of the glass composition (see Table 2). With relatively low oxide concentrations it would require long resident time for the metals to form and then fall to the bottom of the melt. This could be accelerated by the use of a magnetic or gravitational force.

This route has the potential to reduce the level of colorant ions. However, there is only limited work undertaken and further research needs to be conducted.

3.4 Electrochemistry

Electrolytic processing is used widely in minerals beneficiation, environmental decontamination and melt purification industries for plating out particular species from a sludge or solution onto electrodes[57,58,59]. In this process the ions must diffuse to the electrode surface. Usually the solutions used have a low viscosity compared with molten (at 1450°C) soda-lime silica glasses and mass transport is not a significant problem. There are also techniques such as electrode rotation which can reduce the problem. The method has been applied to glass forming melts in order to reduce contamination levels to very low levels but these have been small scale melts of fluoride based glasses, which are much more fluid than silicate based systems.

This approach considers the molten glass as a solution containing metal ions. If a glass at melting temperature is considered, not unreasonably, as a liquid analogous to water, then the application of a DC voltage will cause ionic species to move under the applied potential liberating oxygen and free metals from the metal oxides in the glass. In theory it is possible to attract metal ions to an electrode and, if the EMF could be controlled, to attract only ions of concern such as iron and chromium. Then it would be possible to remove colouring ions from the melt and render the glass clear. The other consideration is the mobility of the ions, due to the relatively high viscosity of the molten glass the ions would move at a relatively slow rate. Practically it would not be acceptable to hold the molten glass at melting temperature for a long period to allow the ions to migrate to the electrode.

While electric melting of glass has been carried out since the 1900's, the need to melt using an AC rather than a DC current has been commercial practice to prevent the erosion of the electrodes by the gases evolved and any free metals liberated under a direct current.

3.4.1 Summary – Electrochemistry

The extraction of metal ions from molten glass is theoretically possible. However, there are practical limitations such as suitable electrode materials and high temperature to reduce glass viscosity. This route has the potential to reduce the level of colorant ions. However, there is only limited work undertaken and further research needs to be conducted.

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[57] S Bao et al, Electrochemical Purification and GFAAS analysis of heavy metal fluoride glass, *J Non-Cryst Solids*, 1995, Vol 184, p194-199.

[58] Pattanayak J et al, Removal of iron and nickel from solutions by application of electrical fields, *Environmental Technology*, Vol 20, No 3, p317-323.

[59] Preparation and characterization of chromium deposits obtained from molten salts using pulsed currents", *J Appld Ekectri.*

3.5 Wet chemical extraction

If glass particles are exposed to a chemical solution it may be possible to preferentially extract colouring ions such as iron and chromium. Mori previously investigated the extraction of silicon dioxide from waste coloured glasses by alkali fusion using sodium hydroxide[60] and potassium hydroxide[61]. The waste glasses were melted via alkali fusion rather than carbonate fusion (ie: Na_2CO_3 at 900°C[62]), as the temperature was lower. The waste glasses selected were green, blue, brown or black and using energy dispersive X-ray spectroscopy were confirmed to contain the following elements: Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe and Cu. The extraction process was based on the following three reactions (as shown for NaOH).

1) Alkali fusion (carried out under optimised conditions – see Table 6)

$$SiO_2 + 2NaOH \Rightarrow Na_2SiO_3 + H_2O$$

Metal hydroxides such as $Mg(OH)_2$, $Mn(OH)_2$ and $Fe(OH)_3$ did not dissolve in the NaOH / KOH silicate solution and were separated from the solution via filtering.

2) Preparation of silicic acid

$$Na_2SiO_3 + 2HCl + H_2O \Rightarrow Si(OH)_4 + 2NaCl$$

3) Preparation of SiO_2

$$Si(OH)_4 \Rightarrow SiO_2 + 2H_2O$$

The results for the fusions are shown in Table 6.

	Optimised conditions	Yield (%)	SiO_2 Purity (%)
NaOH	NaOH : glass 90:10 % mass, 500°C, 2 hrs	98.3	99.9
KOH	KOH : glass 90:10 % mass, 360°C, 2 hrs	97.75	99.9

Table 6 A summary of the fusion conditions and the results obtained for each flux used.

The investigations carried out showed that SiO_2 was extracted from waste glass with a purity of 99.9 % and a yield of > 97 %. It was assumed that KOH would be the preferred flux as the melting temperature of KOH was lower than that of NaOH. The lower melting temperature would result in a lower consumption of energy during fusion, which would lead to a reduction in cost of the recycling process. The author also suggested a method of recycling KCl back into KOH and HCl. The re-use of these materials would lead to a reduction in the cost of the overall process.

The drawbacks to this technique are that it would be time and energy consuming to grind the cullet into small particle sizes, which in turn may lead to problems when re-melting the cullet. However, Drescher[63] claimed that "experience in the glass container industry has shown that no adverse melting behaviour is

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[60] H. Mori, Extraction of silicon dioxide from waste colored glasses by alkali fusion using potassium hydroxide, , Proceedings of the 19th International Congress on Glass, Vol 2. Extended Abstracts, Edinburgh, Scotland, 1-6 July 2001, p12

[61] H. Mori, Extraction of silicon dioxide from waste colored glasses by alkali fusion using potassium hydroxide, *Journal of Materials Science*, Vol 38, 2003, p.3461

[62] M. Mizushima, Kagaku-daijiten Kyoritsu-Shuppan., Vol. 5, 1997, p.720

[63] H Drescher, Grinding Technology improves recycling efficiency, *Glass International*, 1996, p.41

experienced by the use of fine glass powder". Drescher stated that a GlassMax machine could reduce cullet to a powder, which can then be screened to eliminate contaminants.

Rashid[64] used a number of techniques to reduce the oxides of iron and chrome in sand. Via the use of a mechanical separation process along with water washing, attrition and magnetic separation, 70 % of Fe_2O_3 content was removed (Table 7). However, for the sand to be used to manufacture colourless glass a further reduction in Fe_2O_3 was required.

Treatment used	**Fe_2O_3 content (%)**	**Reduction in Fe_2O_3 content (%)**
As received	0.300	-
Water wash	0.121	59.60
Water wash and attrition	0.105	65.00
Attrition	0.110	63.33
Water wash and attrition	0.096	68.00
Water wash, attrition and magnetic separation	0.092	69.33

Table 7 Percentage of Fe_2O_3 content of sand after different mechanical separation processes.

Two different chemical treatments were carried out on the sand that could be applied to extracting Cr & Fe from glass powder, as follows:

3.5.1 Chemical treatment process

Different chemical reagents were used to dissolve the colorants. The different chemical treatment processes that were carried out on the sand are shown in the Table 8.

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[64] A. K. M, Bazlur Rashid, Characterisation and Benefication of the Glass Sand deposits of Bangladesh, Melbourne, Vic, 11th -13th September 2000, p.397

Treatment used	**Fe_2O_3 content (%)**	**Reduction in Fe_2O_3 content**	
		(%)	**(Cumulative %)**
As received	0.300	-	-
Water wash and magnetic separation	0.105	-	65.00
Hydrochloric acid process	0.040	61.14	86.67
Sulphuric acid process	0.045	57.14	85.00
Sodium hydroxide method	0.050	52.23	83.33
Dithionite method	0.037	64.76	87.67
Sulphite process	0.055	47.61	81.67
Adam's process	0.053	49.52	82.33
Sherlock's process	0.042	60.00	86.00

Table 8 Percentage of Fe_2O_3 content after various chemical treatments.

The results show that the most effective process was the dithionite process which reduced the Fe_2O_3 level of water washed and magnetically treated sand from 0.105 % to 0.037 %. The hot hydrochloric acid treatment reduced the level of Fe_2O_3 to 0.040 %.

3.5.2 Froth flotation process

In Rashid[64] work thirteen reagent groups were used in a froth flotation process for the removal of iron and chromium from sand. The results showed that the reagent groups containing sodium laurel sulphonate were the most effective. The Fe_2O_3 and Cr_2O_3 levels were reduced to 0.032 % and 0.0012 % respectively.

The mechanical techniques discussed above are time consuming and would not remove sufficient quantities of the colorants from cullet. The chemical treatment processes would remove a sufficient quantity of Fe_2O_3. However, prior to treatment the cullet would have to be ground which may cause problems during the re-melting of the cullet.

It may be possible to extract sufficient quantities of Fe_2O_3 and Cr_2O_3 from cullet via a froth flotation process. However, further work would be required in this area to determine for example, the most efficient collector. Drawbacks to this technique are that it may be costly, the cullet would have to be ground prior to treatment and it was discovered that the complete separation of iron oxide was difficult.

Harrison[65] discussed the removal of coloured impurities such as titanium and iron oxides from silicate minerals, oxide minerals and clay minerals via a froth flotation technique.

The process was based on the following steps:

1) Preparation of mineral to be purified into a slurry;
2) Pre-condition slurry (addition of flotation chemicals);
3) Condition slurry (addition of chemical collector);
4) Subject slurry to flotation process.

The slurry was preconditioned via the addition of an alkali aluminate compound (eg: sodium aluminate – dosage dependant upon mineral material and average particle size).

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[65] J. M. Harrison, Flotation aid and process for removal of impurities from silicate minerals, United States Patent, 5037543, 6th August 1991

The pH of the slurry was maintained at pH = 8-9 via the addition of caustic soda. The conditioning step involved the addition of a chemical collector (ie: a surfactant) to the slurry. The slurry must be mixed to ensure that the chemical collector and mineral slurry are in contact. The slurry was then subjected to a froth flotation process to ensure the removal of impurities. The research carried out showed that more iron oxide was removed from the clay when an alkali aluminate compound was present.

Mathur et al[66] investigated the removal of titanium oxide from kaolin clay by froth flotation. A hydroxamate was used as a collector at a neutral / mildly alkaline pH. It may be possible to remove Fe and other unwanted colorants from cullet using a method similar to those described above. Although the cullet would have to be ground it may be worthwhile investigating the removal of impurities from cullet via a froth flotation technique.

A number of studies have been carried out to investigate the removal of chromium from various materials. Baturay et al[67] investigated the removal of chromium from chromium containing waste materials. The method was based upon converting chromium to water soluble chromates via a series of reaction steps. The final process, the extraction step, resulted in an aqueous phase containing the soluble chromate and a solid phase containing environmentally acceptable levels of chromium. The author stated that 'Typically about 99.5 % to 99.9 % of the chromium present in the waste material is reacted to water soluble chromates'.

A waste material containing 6 % weight of chromium underwent this process and 99.9 % of the chromium was reacted to sodium chromate. However, 100 ppm of chromium was left in the solid phase.

Glass type:	**Cr (ppm)**
Flint	14
Green	1641
Amber	137

Table 9 Concentration of Chromium present in each type of cullet

The level of chromium in flint glass is ~ 14 ppm. If 99.9 % of the chromium present in green cullet was removed then it may be possible to use it to make flint glass. However, the efficiency of the method discussed above at removing chromium from a material with a low initial chromium content is not known. Lumetta et al[68] investigated the removal of chromium from Hanford tank sludges. The work was based upon the oxidation of Chromium Cr^{3+} (insoluble in alkaline conditions) to chromate Cr^{6+} (soluble in alkaline conditions) using permanganate and O_3. The research showed that chromium was oxidised to chromate using both oxidising agents and that a method was provided for the removal of chromium from an alkaline sludge.

Finally Shen et al[69] investigated the removal of chromium and other metals from tannery sludge using mineral acids. The results indicated that the most suitable acid for the removal of chromium was sulphuric acid and that the pH should be between 1 & 3. The technique's discussed by Baturay et al and Lumetta et al would have to be greatly modified to remove chromium from cullet. They would be both energy and time consuming. Also, it would be much more cost effective to extract the colorants (ie: Fe and Cr) using one technique, rather than removing each separately.

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[66] Mathur et al, Flotation method for removing colored impurities from kaolin clay, United States Patent, 6378703, 30th April 2002

[67] Baturay et al, Method for removing chromium from chromium containing waste material, United States Patent, 5007960, 16th April 1991

[68] G. J. Lumetta et al, Removal of chromium from Hanford tank sludges, *Separation science and technology*, Vol.34, 1997, p.1495

[69] S.B.Shen, Extraction of Cr^{3+} and other metals form tannery sludge by mineral acids, *Environmental Technology*, Vol.22, 2001, p.1007

3.5.3 Summary – Wet chemical treatment

There is only a small volume of literature available on the wet chemical treatment of cullet to enable it to be recycled.

A limitation of the 'wet chemical' route to de-colourise glass is that, prior to treatment, the cullet would have to be crushed into small particles. Not only would this be both time and energy consuming but it may also lead to problems when re-melting the cullet. When small particle sizes are melted, air may become entrapped which can result in the formation of bubbles. However, this may not be a problem for the extraction of SiO_2 from cullet as described by Mori[60,61]. It is thought that small melt trials could be carried out based on this research.

It may be worthwhile investigating the removal of contaminants from cullet via a froth flotation technique. However, this technique would be costly and time consuming.

3.6 Alternative colouring system - Irradiation

It is possible to colour glass by exposing it to x-ray radiation. This is usually a temporary colouration whereby the glass can be returned to the original base colour by thermal treatment.

Sheng et al[70,71] discussed a recyclable glass coloured by x-ray irradiation, with decolouration upon heating. The motivation behind this work was to investigate the technical and economic feasibility of using a reversible colouration mechanism in container glass. Key objectives were to increase colour density and to stabilise the induced colour. Several different glasses were melted, with various small additions such as Fe_2O_3, P_2O_5, Ag_2O, CoO and CuO. X-ray irradiation induces defects in the glass structure that in turn affect the optical characteristics of the glass.

Commercial colourless container glass was used as a benchmark. Upon x-ray irradiation it darkened to a deep brown, with this colour easily bleached with heat treatment. It was possible to distinguish 2 main absorption bands in the darkened glasses, centred at 440nm and 620nm.

Even if stored in the dark at room temperature, the induced colour faded rapidly over the first few days, then faded more slowly. Clearly the induced colouration was highly unstable in the undoped glass[72]. It was noted that this induced colour was neither so stable nor as deep as with commercial amber glasses. In particular, glasses doped with small amounts of silver[70] ($\approx$ 0.02 wt% Ag_2O) improved the colour depth very strongly, such that even after 10 months under ambient atmosphere, the colour was still stronger than in commercial amber glass.

It was found that most of the colour in the base glass could be removed by heating to 200°C, and almost totally disappeared at 300°C for 20 minutes. To completely remove the colour required 500°C for 20 minutes. It therefore appears that with the correct doping it may be possible to make recyclable flint glasses which can outperform most amber glasses. This is a very positive piece of work, and whilst it does not strictly fall under the "in the furnace" category, it is still relevant and deserving of further investigation. If such glasses could be coloured green under irradiation rather than brown, this would be an additional benefit. However, little evidence of the creation of green colouration by irradiation could be found.

Paymal et al[73] discussed the effects of ionising radiation on glasses doped with combinations of Mn-Fe, Mn-V, and Mn-V-Fe. These glasses utilised the fact that oxidation of Mn^{2+} to Mn^{3+} by photooxidation gives rise to a colour change. Irradiation of glass containing 0.4% MnO and 0.13% Fe_2O_3 showed a huge increase in colour, from a weak decolourised iron colour, to a strong manganese purple/indigo colour, with a large, broad absorption band centred at 540 nm.

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[70] J. Sheng et al, Easily recyclable coloured glass by x-ray irradiation and colouration, *Glass Technol.*, Vol. 43, No. 6, 2002, p. 238.

[71] J. Sheng et al, X-ray irradiation on the soda-lime container glass, *App. Radiation Isotopes*, Vol. 57, 2002, p. 813.

[72] J. Sheng et al, Fading behaviour of X-ray induced colour centres in soda-lime silicate glass, *App. Radiation Isotopes*, Vol. 56, 2002, p. 621.

[73] J. Paymal et al, Radiation dosimeter glasses, *J. Amer. Ceram. Soc.*, 1960, Vol. 43, No. 8, p. 430.

Various other workers have investigated the effects of irradiation on glasses, including dosimeters[74], gamma radiation - induced colour in quartz[75,76], electron bombardment[77], and a good general paper on radiation induced colour centres in glass[78].

El-Hadi[79] discussed the interaction of gamma radiation with lead borate and lead silicate glasses doped with low levels (0.05%) of Cr_2O_3. Results were very interesting, as they implied that irradiation resulted in strengthening of the characteristic Cr absorption bands. It seems more likely that broad absorptions were superimposed over the existing ionic absorptions.

El-Batal[80] undertook an extensive series of experiments on ternary silicate glasses doped with CoO & NiO, it was found that any colouring ion would exhibit a stronger colouring effect after irradiation. It was reported that both the chemical and mechanical properties will change with varying extent. However, this was not quantified and therefore is an area for further research.

An implication of this work is that if some combination of colorants and irradiation were used, it may be possible to maintain the required green colour of iron-chromium glasses, but using substantially less iron and chromium, with a “top-up” consisting of irradiation.

The evidence presented in these papers demonstrates that high-energy irradiation of glasses usually results in the formation of colour centres which have very broad absorptions. Often these colours are brown in tone, due to the positions of the absorption bands which can occur throughout the visible spectrum at various strengths.

No evidence was found to suggest the possibility of forming a green colour by any irradiation method on its own, although as discussed previously, Sheng et al have suggested that it may be possible to use this method for amber colours, and El-Hadi’s method may make it possible to form green colours using a combination of colorants and irradiation, resulting in lower iron and chromium levels needed in the glass. This in turn could allow higher levels of this cullet in flint glass.

Irradiation of existing glasses shows no evidence for potential colour removal or “bleaching” effects. Indeed, glasses of the 3 main colours which have been subjected to X-Rays in an XRF spectrometer shows deeper colours after irradiation. Interestingly, by far the strongest increase in colouration is found in flint glasses, which go from clear to grey/brown upon irradiation. In amber glasses the colour only deepens and in green glasses there is little discernible change in colour (to the eye) before and after irradiation.

This is yet further evidence to back up the conclusion that it will be unlikely that the colours we are dealing with in green and amber glass can be removed by irradiation. If the colours were initially caused by irradiation, rather than by dissolved components of the glass, this appears to be a much more promising line of investigation, backed up by significant evidence from the literature.

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[74] W. A. Hedden et al, Investigation of some glasses for high-level gamma-radiation dosimeters, *J. Amer. Ceram. Soc.*, 1960, Vol. 43, No. 8, p. 413.

[75] P. W. Levy, Reactor and gamma-ray induced colouring of Corning fused silica, *J. Phys. Chem. Solids*, 1960, Vol. 13, p. 287.

[76] C. M. Nelson & R. A. Weeks, Trapped electrons in irradiated quartz and silica: I, optical absorption, *J. Amer. Ceram. Soc.*, 1960, Vol. 43, No. 8, p. 396.

[77] T. M. Mike et al, Effect of electron bombardment on properties of various glasses, *J. Amer. Ceram. Soc*, 1960, Vol. 43, No. 8, p. 405.

[78] A. Bishay, Radiation induced colour centres in multicomponent glasses, *J. Non-Cryst. Solids*, 1970, Vol. 3, p. 54.

[79] Z. A. El-Hadi, Gamma-ray interaction with some high-lead glasses containing chromium ions, *J. Solid State Chem.*, Vol. 163, 2002, p. 351.

[80] F.H.A. El-Batal, Gamma rays interaction with ternary silicate glasses containing mixed CoO + NiO, *Mater. Chem. Phy.*, Vol. 82, 2003, p. 375.

3.6.1 Summary - Irradiation

Irradiation is not a colour reduction route, however, it is a process of introducing a colour to a clear glass. There is currently active research, mainly by a Japanese group, into the use of irradiation as a colouring mechanism, with the potential to increase glass recycling.

This route has the potential to only produce flint glass that is coloured by irradiation. However, there is only limited work undertaken and further research needs to be conducted.

3.7 Summary & Conclusions

At this stage only the technical feasibility has been investigated and all the routes discussed are technically possible. However, all the routes have some practical and economic limitations that need to be addressed with further research and development.

In the short term the dilution and decolourising route has the most potential. The wet chemical route has the potential to produce high quality materials for glass melting or alternative applications. The process of irradiating clear glass to produce the desired colour is an exciting solution but there are many barriers to overcome, from commercial to practical.

4 Practical Investigation

Based on the literature review it was agreed that further laboratory investigations are required. Due to the limited timescale of this project only the following were investigated:

- Dilution, decolourising & colour balance;
- Reductive melting;
- Wet chemical extraction;
- Alternative colouring system - Irradiation.

Due to the complexity of equipment it was not possible to investigate the following within the scope of this project:

- Crystallisation and phase separation;
- Electrochemistry.

4.1 Dilution, Decolourising & Colour Balance

It was identified that dilution, decolouring & colour balance was possibly an approach that could allow the introduction of mixed glass into flint or amber melts. Therefore, a series of experiments were devised to further investigate work reported in the literature.

4.1.1 Laboratory Melts – Commercial Raw Materials

All the experiments were conducted under laboratory conditions; these were 200g melts in an electric radiant heat furnace. Unfortunately, this scale of melting has different conditions such as redox and heat distribution, compared to full scale melting in a container tank furnace melting in excess of 200 tonnes per day. However, these laboratory melts were considered indicative of the potential for a full scale melt.

In the series of melts undertaken commercial batch materials and recipes were used, to simulate the composition and batch chemistry of commercially produced container glass.

Series Code	% Green Addition
GF0	0
GF1	0.5
GF2	0.75
GF3	1
GF4	2.5
GF5	5
GF6	7.5
GF7	10

Table 10 Green cullet additions (in final glass) to flint batch materials.

Series Code	% Green Addition	Decolouriser Ratio
GF/D1	0.25	0.2
GF/D2	0.5	0.3
GF/D3	1	0.4
GF/D4	0.5	0.5
GF/D5	1	1
GF/D6	5	5
GF/D7	10	10

Table 11 **Green cullet additions (in final glass) to flint batch materials with decolouriser additions to compensate for the Cr & Fe colouring ions.**

Series Code	% Green Addition	% Amber Addition
1% A-F		1%
5% A-F		5%
10% A-F		10%
1% G-F	1%	
5% G-F	5%	
10% G-F	10%	

Table 12 **Series of glasses with green and amber cullet additions to flint glass.**

All the above compositions were melted in ceramic crucibles for 4 hrs at 1450°C (excluding temperature ramp up) the melts were cast into 100 x 30 x 10 mm blocks and polished on two faces (between 10 mm faces). Then ultraviolet to visible light spectrometry was undertaken on each sample to determine the colour coordinates. The colour coordinate system used was the CIE L*a*b* Colour space which is suitable for faint colours in glass. The L*-axis is known as the lightness and extends from 0 (black) to 100 (white). The other two coordinates a* and b* represent redness-greenness and yellowness-blueness respectively. Samples for which a* = b* = 0 are achromatic (colourless) and thus the L*-axis represents the achromatic scale of greys from black to white. Figure 4 shows the a & b coordinates that depict colour and the L is the vertical axis (z).

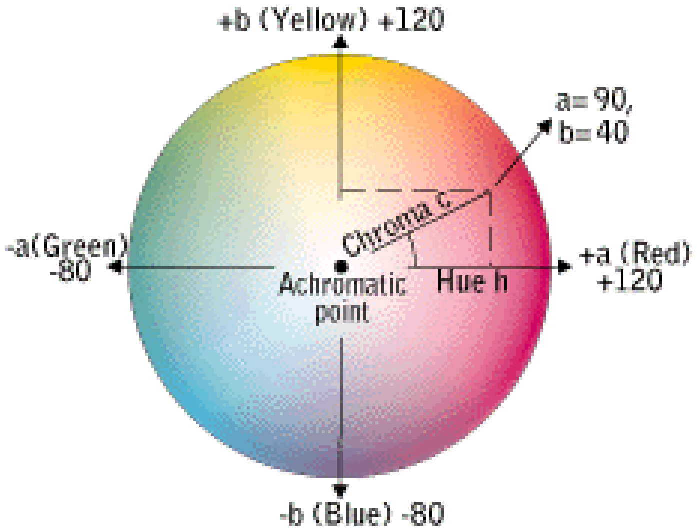


Figure 4 **CIE colour space reference chart.**

4.1.1.1 Results & Discussion

All the melts undertaken produced acceptable glass quality that was suitable for colour measurements. Also there were no noticeable defects associated with glass melting such as bubbles and non-melted batch materials.

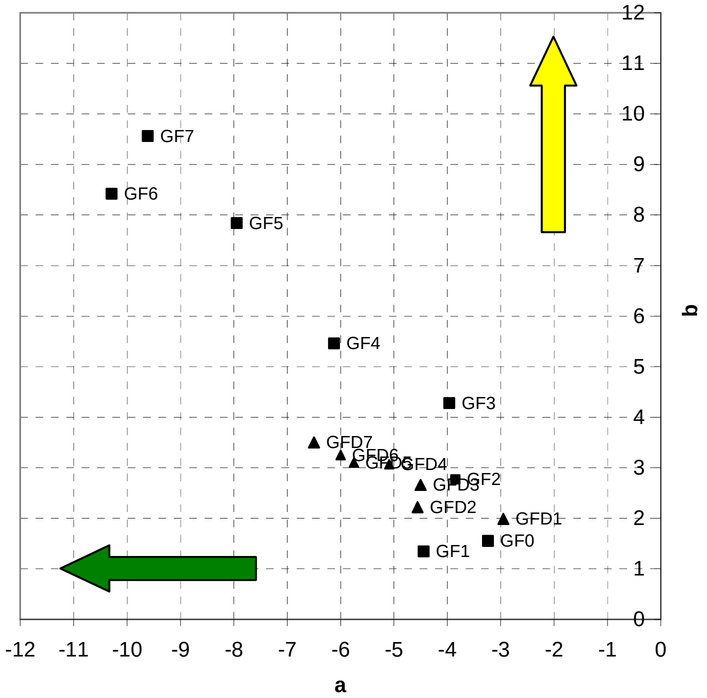


Figure 5 **CIE colour space measurement for the GF# and GFD# series (tables 10 & 11 respectively).**

Glass GF0 was made from raw materials with no cullet additions which had very similar colour to GFD1, a glass that represents a typical flint container glass. As the cullet addition was increased towards 10% (GF7) the colour moved towards the green/yellow. With the GFD# series it was possible to suppress the green/yellow colour with the use of selenium as a decolouriser. The effect of the decolouriser additions can visually be appreciated in Figure 7. Also the L value for the GFD1 to GFD4 (85-90) series was of a similar value to the corresponding GF series.

From GFD5 to GFD7, 1% & 10 % green cullet respectively, the L value decreased slightly (75-85) as expected. This was a function of the high level of decolouriser resulting in loss of light transmission. In particular the GFD7 glass had a slight grey appearance due to light absorption.

Figure 6 shows the absorption peaks (negative peaks) for chromium (10% green) at 450 & 650 nm. As the chromium level increases so does the adsorption at 450 & 650 nm giving a glass that appears green. The 10% amber transmission does not show the expected absorption peak at 1100 nm due to equipment limitations.

The experiments were limited and further experimental work is required to determine the most suitable decolouriser for flint container glass with above average green cullet additions.

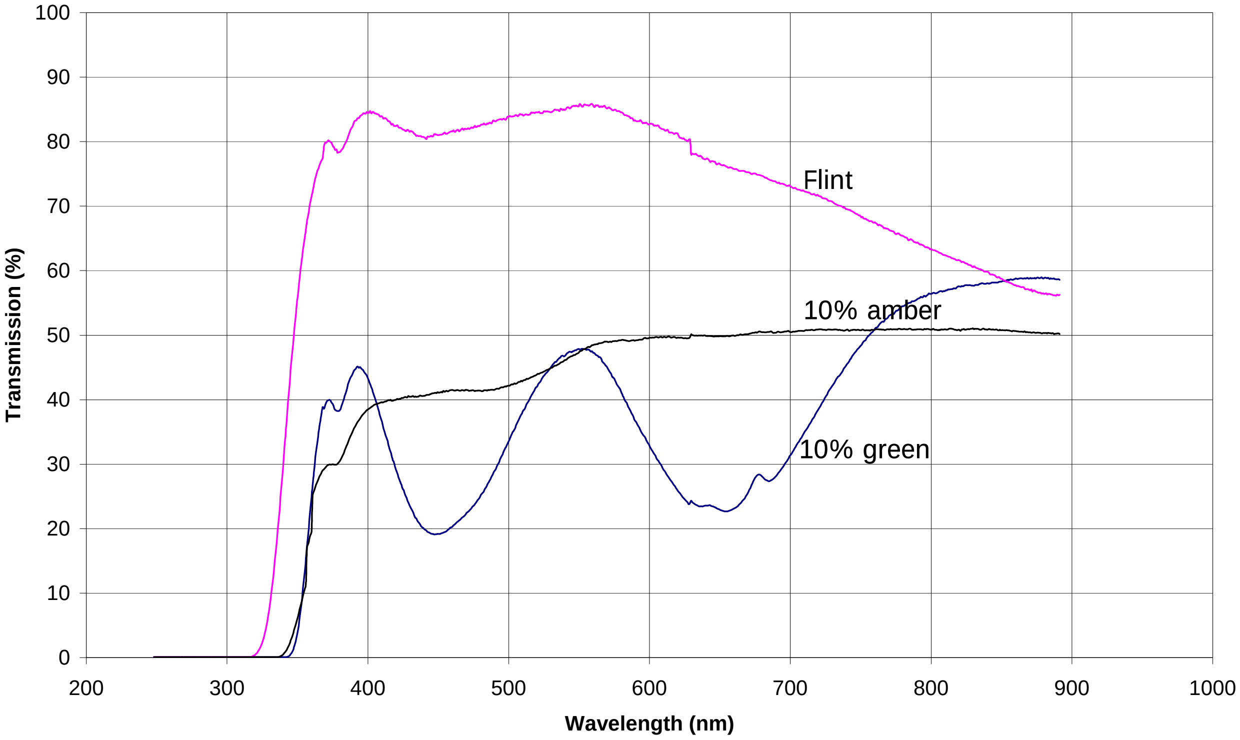


Figure 6 Transmission curve of flint, flint + 10% green and flint + 10% amber.

Series GF – Based on Commercial Glass Compositions

Series GFD – Based on Commercial Glass Compositions with Increased Decolouriser

Figure 7 **Visual comparison between the GF# & GFD# series of glass samples.**

The addition of amber cullet to flint batch materials had a less predictable impact compared to the GF & GFD series. This was due to the problems of replicating redox conditions of a container furnace with small melts in an electric furnace. But as expected the colour shifts was towards the yellow and away from the green towards the red. Amber glass has a Cr content 10x greater than flint, whereas green has a Cr content 100x greater than flint. Considering the Cr is a stronger colorant than Fe in glass, this suggests that there is more potential to use amber cullet in flint glass.

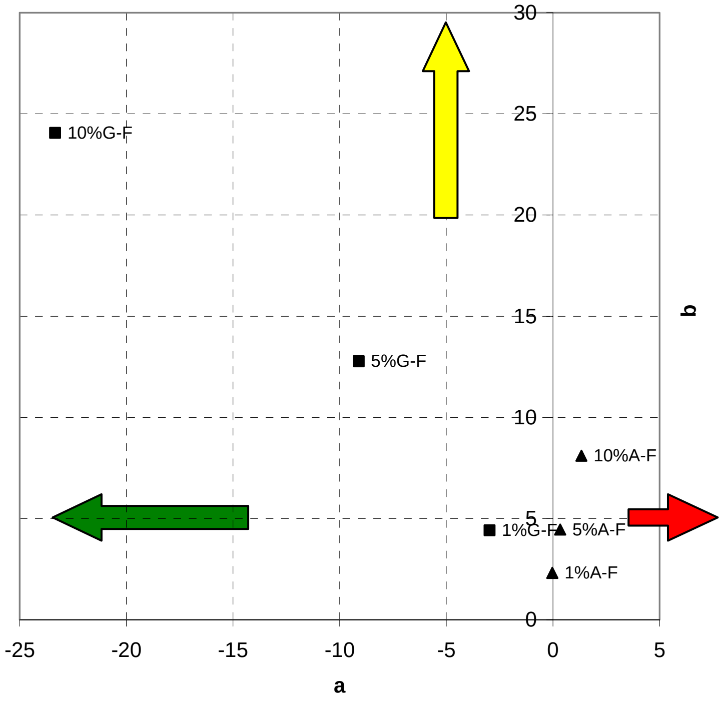
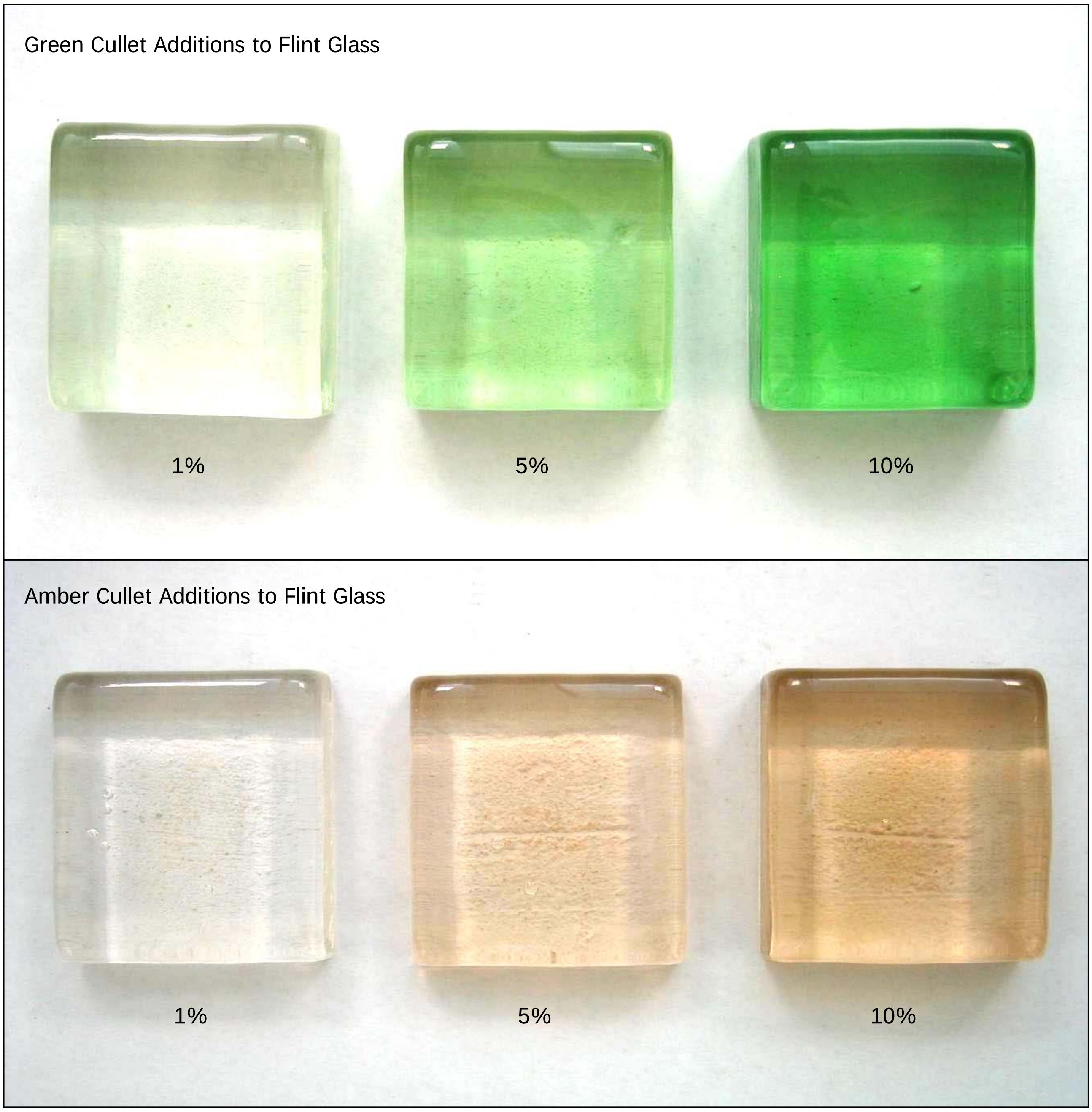


Figure 8 **CIE colour space measurement for series of melts with additions of coloured cullet to flint cullet (Table 12).**


Green Cullet Additions to Flint Glass

Amber Cullet Additions to Flint Glass

Figure 9 **Visual comparison between series of glasses with green and amber cullet additions to flint glass.**

A series of melts (Table 12) was undertaken to indicate the effect of mixing coloured cullet with flint glass, no decolouriser was used. Figure 8 shows that 1% green glass added to flint glass results in a glass that is strongly coloured and would require high levels of decolouriser to mask the colour. On the other hand the amber cullet has a lesser effect, moving the colour toward the yellow/red (brown). Therefore, flint glass melts could tolerate higher levels of amber cullet additions. The colouring effect can be visually seen in Figure 9.

Addition series of melts were undertaken to demonstrate the impacted of using mixed colour glass in flint glass melts. The results are visually shown in Figure 10.

Figure 10 **Visual comparison of a series of glasses with mixed cullet additions to flint glass and a glass sample with 100% mixed coloured glass.**

4.1.2 Laboratory Melts – Controlled Melts

In addition to the melts described in section 4.1.1, a series of melts were undertaken using analytically pure raw material to further investigate the affect of Cr_2O_3 on simple glass structures.

Therefore this series was designed to examine the following:

1) To consider whether melting under oxidising or reducing conditions can eliminate the associated colour;
2) To assess what limit of dopants contribute noticeably to the finished product;
3) To investigate whether the colour can be eliminated by adding other colorants which give rise to continuous absorption over the whole spectrum i.e. a grey colour.

Six series of glasses were melted as follows:

1) To assess what level of green cullet was likely to give a noticeable level of coloration.
2) To test the effect of adding oxidising and reducing agents.
3) Similar to 2 but for amber glass.
4) To test the addition of nickel and cobalt oxides to try to balance out the colour introduced by chromium.
5) To assess the effect of different redox conditions on the Cr and Fe absorption peaks.

6) To assess the effect of MnO (added as $KMnO_4$) and reducing agents on the Cr and Fe absorption peaks

A list of actual batch compositions melted is given in Table 13 to Table 18.

The batches were weighed out to an accuracy of 0.01g for the major components and to 0.001 g for the minor components. The raw materials used consisted of low Fe sand, limestone and soda ash. Other materials were all analytical grades to avoid inclusion of unknown quantities of colorants. Melting was carried out in mullite crucibles that showed some evidence of corrosion after melting was complete suggesting that alumina and silica contents of the final glass may have differed slightly from the batch compositions. While alumina can slightly affect the observed colour the effect is expected to be very small. Some iron contamination may also be introduced.

Melting was carried out in a gas-fired furnace at 1450°C. Melting continued for 5 hours after which time the glass was cooled to a suitable temperature for casting. The glasses were cast as discs and then annealed at 550°C.

Glass specimens obtained were found to be well annealed and homogeneous by examination visually and in a strain viewer, but contained a low level of seed. They were cut into samples measuring 2x3 cm^2 and polished. The prepared samples were examined using a IR/Vis/UV Spectrophotometer. Absorption spectra were recorded over the range 200 nm to 3000 nm. Apart from the specimens melted, some glass samples from commercial bottles were also examined.

Glass	1A	2A	3A	4A	5A	6A
SiO_2	72	72	72	72	72	72
Na_2O	15	15	15	15	15	15
CaO	13	13	13	13	13	13
Added	0	0.01% Cr_2O_3	0.02% Cr_2O_3	1% cullet	2% cullet	5% cullet

Table 13 **Series A - Compositions in wt %. 300g batches melted. Colorants introduced as an addition to basic 300g batch. 97% of Na_2O introduced as Na_2CO_3, the rests Na_2SO_4. Green cullet added.**

Glass	1B	2B	3B	4B	5B	6B	7B
SiO_2	216	216	216	216	216	216	216
Na_2CO_3	76.95	76.95	76.95	76.95	73.11	73.11	69.26
Na_2SO_4	0	0	0	0	5.16	0	0
$NaNO_3$	0	0	0	0	0	6.17	12.34
$CaCO_3$	69.61	69.61	69.61	69.61	69.61	69.61	69.61
Amber cullet	0	3	6	15	15	15	15

Table 14 **Series B - All the compositions melted had the same base composition as given in Table 13. In some cases soda was added as the nitrate (6 and 12% replacement) to provide oxidising conditions and in other cases as sulphate. Amber glass cullet was added at different levels to a batch corresponding to 300g of glass to assess how much could be added without detriment to the finished product.**

Glass	1C	2C	3C	4C	5C
SiO_2	216	216	216	216	216

Na_2CO_3	74.64	74.64	74.64	72.34	70.03
Na_2SO_4	3.09	3.09	3.09	3.09	3.09
$NaNO_3$	0	0	0	3.70	7.41
C	0	1	2	0	0
$CaCO_3$	69.61	69.61	69.61	69.61	69.61
Cr_2O_3	0.3	0.3	0.3	0.3	0.3

Table 15 **Series C - Glasses based on a standard base glass with 0.1 wt% chromic oxide but varying levels of oxidising and reducing agents.**

Glass	1D	2D	3D	4D
SiO_2	216	216	216	216
Na_2CO_3	76.95	76.95	76.95	76.95
$CaCO_3$	69.61	69.61	69.61	69.61
Cr_2O_3	0.06	0.06	0.06	0.06
NiO	0	0.06	0.12	0.18
Co_2O_3	0	0.06	0.03	0.03

Table 16 **Series D - Glasses with added levels of other transition metals designed to produce a neutral shade.**

Glass	1E	2E	3E	4E	5E	6E
Cr_2O_3	0.25	0.25	0.25	0.25	0.025	0.0025
Fe_2O_3	0.03	0.07	0.1	0.2	0.1	0.01

Table 17 **Series E - Glasses based on 72 wt% SiO_2, 13.4 wt % Na_2O, 10.9 wt % CaO, 0.4 wt % K_2O, 1.7 wt % MgO and 1.25 wt % Al_2O_3 to investigate the effect of redox conditions on Cr & Fe peaks.**

Glass	1F	2F	3F	4F	5F	6F	7F
Cr_2O_3	0	0	0	0	0	0	0
Fe_2O_3	0.1	0.1	0.1	0.1	0.1	0	0.3
MnO	0.1	0	0.3	0.3	0.3	0.3	0
Reducing agent-sugar	0	0	0	0	1g	2g	0

Table 18 **Series F - Glasses based on 72 wt% SiO_2, 13.4 wt % Na_2O, 10.9 wt % CaO, 0.4 wt % K_2O, 1.7 wt % MgO and 1.25 wt % Al_2O_3 to investigate the effect of MnO and reducing agent (sugar).**

4.1.2.1 Results and Discussion

The spectra for the commercial green glass show peaks at 450 nm and 650 nm, together with a broader peak at 1100 nm and a final peak at 2900 nm. Amber glasses showed a broad absorption from 200 to 550 nm with a further peak at 1100 nm.

The spectra were identified by comparison with those shown in Weyl[10]. The peaks at 450 and 650 nm belonged to chromium, a widely used colorant for green glass and the brown glasses had an absorption profile consistent with that for O_3^{2-}-Fe^{3+}-S^{2-} complexes. The peak at 1100 nm belongs to ferrous (Fe^{2+}) iron; iron is a widespread contaminant of many raw materials and a deliberate additive for amber glass.

The commercial green bottles all had chromium as the principal colourant at a concentration of approximately 0.25 wt%. More surprising was the significant level of ferrous iron in these specimens, suggesting that perhaps lower grade sand was used in the melting process or possibly that chromium was introduced as an iron containing mineral e.g. chromite. Higher levels of iron can be tolerated since this specie also tends to colour the glass green, although it does not produce such a sharp transmission band. Iron is also added to green glass to produce the colour known as Feuille Mort. It may also have the advantage of decreasing the UV transmission. The consequence however is that when reducing conditions were studied, an amber glass resulted. Also it suggests that not only must the green of chromium be removed but also the role of iron as a contaminant must be considered.

Studies on the effect of determining the acceptable level of cullet (Table 13) showed that even a 1% green glass cullet addition gave a noticeable green colour to the glass compared with the standard made by melting with standard grade chemicals. This result is consistent with the reported normal acceptance limits of 0.3% for green glass contamination of flint cullet (0.001 wt % Cr). The pale green glasses with 0.02% Cr_2O_3 were perceived as particularly attractive.

On the other hand additions of amber cullet (Table 14) gave flint glasses showing very little colour other than that associated with low iron concentrations even with additions of 10 wt% cullet. Amber requires the presence of 2 species namely Fe^{3+} and S^{2-}. The intensity of the induced colour might therefore be expected to vary as $[Fe^{3+}][S^{2-}]$ i.e. to decrease as $[\text{cullet concentration}]^2$ where the cullet is the main source of iron and sulphur. In reality there will also be iron in the batch and any flint cullet and sulphur may also be introduced from these sources so the effect of dilution will be less pronounced.

The series of glass samples C show the effects of reducing and oxidising conditions on the Cr absorption peaks in a green glass. Under reducing conditions the height of the Cr^{3+} corresponds closely with the added concentration. Under strongly reducing conditions an amber colour is produced in addition to the overall green shade as a result of the high iron levels in the sample. The origin of this iron is unclear since pure chemicals were used but it may have arisen in part as a result of contamination by the crucible. The sulphur required originates from the refining agent used. Since green glasses often contain significant iron levels the same effect may be a problem if using contaminated cullet. The glasses melted under oxidising conditions have slightly reduced Cr^{3+} levels (but the change is barely significant) and show evidence of a Cr^{6+} absorption at shorter wavelengths. The reduction in Cr^{3+} concentration is however very small and this result is consistent with an observation in Weyl[10] who reported a reduction of 18% in Cr^{3+} when melting under oxidising conditions. Here the effect is smaller than that. The Cr^{6+} produced is itself a strong colourant, absorbing in the near UV and giving the glass a yellow colour. This effect may be an advantage in reducing UV transmission but Cr^{6+} is generally regarded as unacceptable because of its associated carcinogenic properties.

Experiments to produce a balanced grey by adding further colorants were partially successful. Additions of both cobalt and nickel were investigated; these showed that even when present in low concentrations cobalt tended to introduce a blue tinge and to make the glass too dark – the effect of nickel was more beneficial, producing a more neutral colour but more work is needed – even low concentrations of these additives gave the glass too strong a colour to be useful.

A further consideration is that the introduction of coloured cullet will slowly contaminate the flint glass stream and if large fraction of the glass is recycled contamination levels will slowly rise as shown in Figure 1.

Series E glasses demonstrated that Cr^{6+} will strongly oxidise iron to the ferric state. In all the glasses with 0.25 wt% Cr there is no ferrous peak visible even though up to 0.1 wt% iron was added. Only as the proportion of Cr is reduced to below the iron concentration does the ferrous peak appear. They also point to the importance of the iron concentration in a green glass in ensuring that Cr^{6+} is reduced to Cr^{3+}.

The series F glasses were melted to discover the effect of different conditions on iron rather than chromium, since the iron itself is a contributor to the green hue of chromium doped glasses. These samples showed a wide range of shades depending on the proportions of the different species added. 0.3wt% Mn on its own produced a slightly purplish hue. With 0.1% Fe present the glass was yellow indicative of the result that most of the iron had been oxidised to the ferric state. By adding different levels of reducing agent these glasses could be reduced to firstly a blue corresponding to significant Fe^{2+} concentrations and finally an amber. The glass with 0.1 wt% Mn and Fe was possibly slightly less green than without the Mn i.e. low levels of manganese did succeed in enhancing the glass transparency. Clearly in any study to examine the possibility of decolourising glasses containing both iron and chromium the interactions between the different species present will be key considerations.

4.1.2.2 Conclusions

1) Chromium is a very persistent and intense colorant which is not significantly affected by oxidation or reduction nor can it can be easily masked by other additives
2) The amber chromophore is much less stable since it involves sulphide ions and significant levels of amber glass can be present in the cullet, although contributing to the total iron level in the glass
3) If sulphate is used as a refining agent reducing conditions may produce an amber because of high iron levels in both green and amber glasses
4) The pale green glass colour produced at about 5-10% of the normal Cr level was regarded as particularly attractive.
5) Indeed it has shown the importance of the iron content of these glasses in ensuring a low Cr^{6+} content in the final glass and that interactions between different redox ions will be an important factor when designing decolourising systems.
6) The colour of the added iron can be partially bleached using a variety of redox pairs including the Mn^{3+}/Mn^{2+} system but other similar systems such as Ce^{4+}/Ce^{3+} are also known to be effective.

4.2 Reductive melting

It was reported in the literature that metallic silicon could reduce Cr and Fe from the glass matrix to form a metallic alloy particle. It is known that aluminium will reduce SiO_2 to Si, therefore, a series (Table 19) of melts were conducted using both metallic Al and Si.

Series	Addition	Particle size	Glass colour
RM 1	Si particle	5 mm	Green
RM 2	Si 0.5 %	fine	Green
RM 3	Si 1%	fine	Green
RM 4	Si 1%	fine	Mixed
RM 5	Al 0.5%	fine	Green
RM 6	Al 1%	fine	Green

Table 19 Series of laboratory melts using metallic additions to cullet.

The laboratory melts with undertaken using 200 g of finely ground cullet (≈1 mm) melted in pure alumina crucible in a radiant heat electric furnace. With RM 1 the Si particle was placed near the top cullet. For other melts (RM 2 to RM 6) the metallic powder was evenly distributed in the cullet. The melts were conducted for 4 hours at 1400°C with initial temperature ramp of 3 hours. The melts were cast into blocks and then samples were taken to reveal the metallic inclusions.

4.2.1 Results

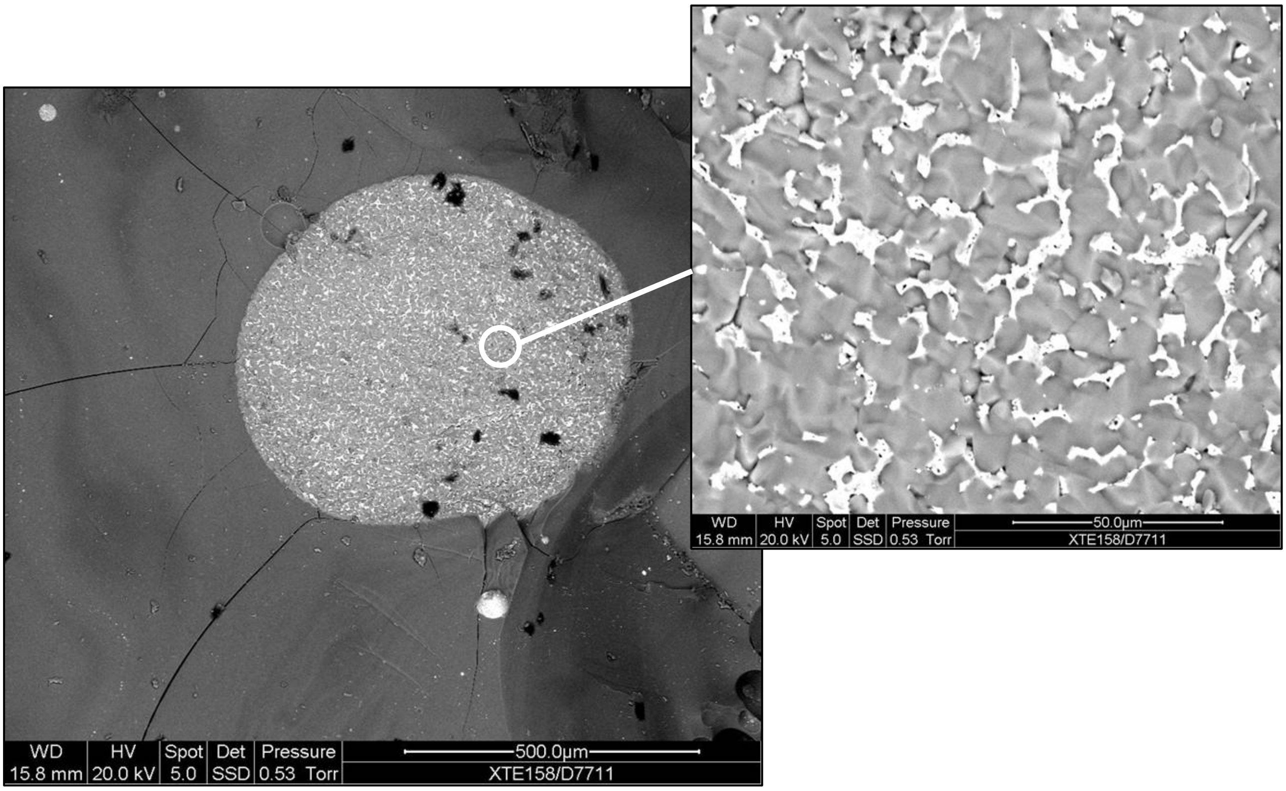


Figure 11 **Metallic sphere representing a 1% fine silicon powder addition (sample RM3) to a green glass melt.**

Figure 11 shows a silicon particle that has two distinct phases; the grey light phase is pure silicon metal and the light phase is silicon rich with Cr & Fe that has diffused from the glass. The elemental analyses of the grey and light phase are shown Figure 12 & Figure 13 respectively. However, even though there appears to be Cr & Fe diffused into the metallic sphere, the glass still contained significant quantities of Cr & Fe. To minimise the oxidation of the silicon the melt was kept under reducing conditions, which did not allow the glass colour to lighten. Figure 14 shows two samples from the melting experiments, it can be clearly seen, especially with the silicon metallic additions that the glass colour and quality would not be acceptable.

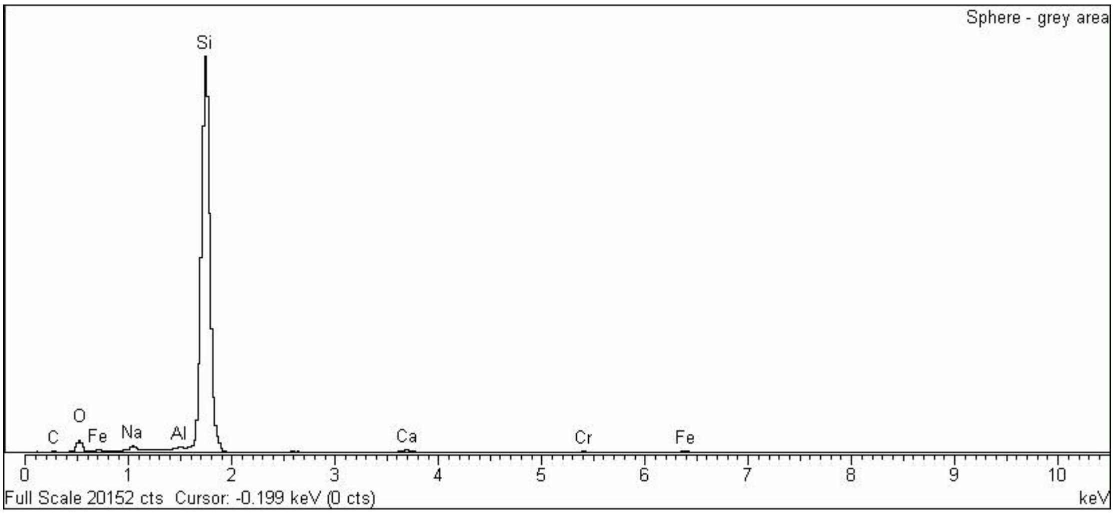


Figure 12 **Elemental analysis of the grey phase.**

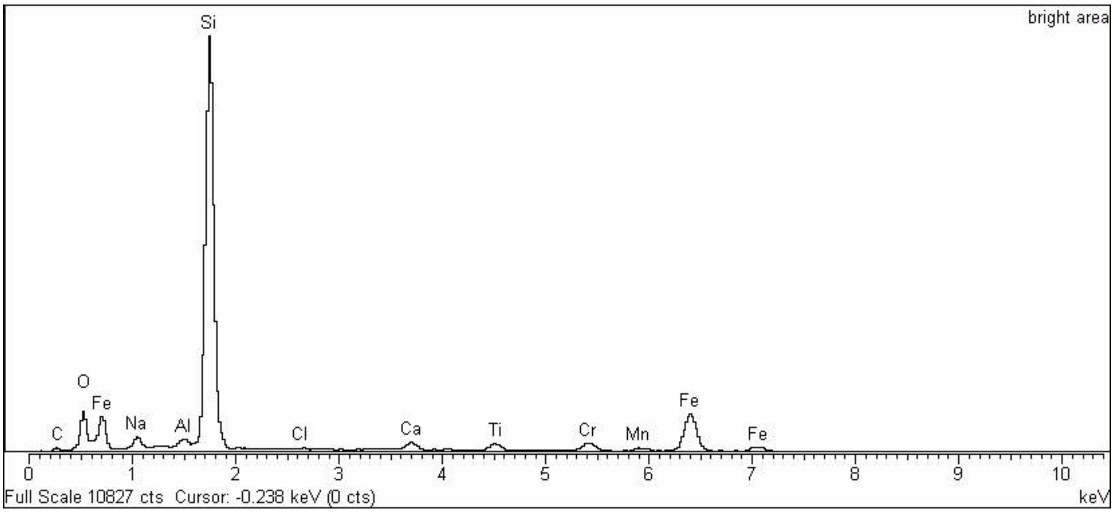


Figure 13 **Elemental analysis of the light phase.**

It is known that metallic Al will reduce SiO_2 to metallic silicon; therefore, small quantities of Al were added to a green glass melt. This produced small spheres of Si in the vicinity of the Al, with a similar composition to the sphere shown in Figure 11.

1% silicon metal addition

1% aluminium metal addition

Figure 14 **Reductive melting samples with 1% silicon and 1% aluminium fine metal particle additions into the glass melt (green glass).**

4.3 Wet chemical extraction

Two set of practical experiments were undertaken to verify the reported claims found in the literature, these being:

Alkali Fusion	Extraction of high purity silicon dioxide (sand or SiO_2) from cullet. The experiment was based upon work previously performed by Mori[60,61], as highlighted in the literature survey.
Acid Washing	The removal of Fe and Cr from finely ground glass using a series of acid washes.

The experiments undertaken were carried out on both green and amber cullet. The cullet was sampled, washed with deionised water and left to dry in an oven at 100°C for 1 hour. An agate lined planetary mill was used to grind the cullet to a size fraction $< 100\ \mu m$.

A semi quantitative XRF analysis was carried out on both cullet samples to determine an approximate weight % of the analytes present. The results of the analysis are shown in Table 20.

Analyte	Green Cullet (Weight %)	Amber Cullet (Weight %)
SiO_2	69.96	70.89
Na_2O	14.33	14.28
CaO	11.15	11.28
MgO	1.21	0.68
Al_2O_3	1.92	1.66
K_2O	0.65	0.78
Cr_2O_3	0.247*	0.018*
Fe_2O_3	0.345*	0.284*
SrO	0.04	0.02
ZrO_2	0.04	0.05

Table 20 A semi quantitative XRF analysis of the green and amber cullet. *Determined using wet chemical colourimetric techniques.

4.3.1 Alkali Fusion - Extraction of Silicon Dioxide (SiO_2)

A platinum dish containing a mixture of 5 g cullet and 45 g of potassium hydroxide (KOH) was melted in a muffle furnace at 360°C for 2 hrs. The fusion was left to cool, and then digested in 600 ml of water to produce potassium silicate solution. The solution was filtered and, under an atmosphere of argon, concentrated HCl was added to the solution to obtain a $pH < 1$. The acidified solution was boiled until a precipitate was formed. The HCl and H_2O vapours were condensed and collected in a beaker.

The precipitates of KCl and $Si(OH)_4$ were filtered and heated to dryness. SiO_2 was produced upon heating the $Si(OH)_4$. After the addition of water, SiO_2 (solid) and KCl (aqueous) were separated by filtration. Finally the SiO_2 was rinsed with warm HCl, warm deionised water and then dried in an oven at 300°C for 2 hours. The percentage purity of SiO_2 was determined by 'loss on HF'.

4.3.1.1 Results

Sand A and sand B were 99.8 % and 99.9 % SiO_2 respectively. The results are shown in Table 21.

Sand	Weight of SiO_2 extracted	Size Fraction	% Yield	% Purity of SiO_2	% Fe_2O_3	% Cr_2O_3
A (green)	2.3786 g	< 200 μm	68	99.84	0.003	0.0004
B (amber)	2.7975 g	< 200 μm	79	99.92	0.004	0.0005

Table 21 Analysis of sand extracted from green and amber cullet.

The colour of the extracted sand was also an indication of the purity. Sand A was pale beige in colour, whilst sand B was pale cream (Figure 15). Hence, sand B was of a higher purity than sand A, which was in agreement with the results stated above. The extracted sands were analysed for Fe_2O_3 and Cr_2O_3. The results show that sand A contained 30 ppm Fe_2O_3 and 4 ppm Cr_2O_3 whilst sand B contained 40 ppm Fe_2O_3 and 5 ppm Cr_2O_3.

Previous work carried out by Mori reported to have extracted sand with a yield of 99.75 %. The average % yield extracted during these experiments was 73.5 %. This average could be improved upon with further development of the process.

Figure 15 **Sands from green (sample A) and amber (sample B) cullet produced by the alkali fusion route.**

4.3.1.2 Conclusion

High purity sand was extracted from both green and amber cullet. The extracted sands were analysed wet chemically for Fe_2O_3 and Cr_2O_3 and were found to contain the following results:

Sand extracted from:	% Fe_2O_3	% Cr_2O_3
Green cullet	0.003 (0.345)	0.0004 (0.247)
Amber cullet	0.004 (0.284)	0.0005 (0.018)

Table 22 **Analysis of remaining Fe_2O_3 & Cr_2O_3 in the sands produced, numbers in ( ) are the levels of Fe_2O_3 & Cr_2O_3 before the fusion process.**

Due to time constraints it was not possible to repeat the experiment to obtain a sufficient amount of sand for a large scale melting trial. However, if a sufficient quantity of sand was extracted it would be worthwhile to carry out a trial melt to produce glass samples. The glass thus produced could be analysed for trace level contaminants.

The recommended chemical composition of sands used for glassmaking sands are shown in Table 23.

Analyte	Optical and ophthalmic glass	Tableware and lead crystal glasses	Borosilicate glasses	Colourless container glass	Flint flat glass	Coloured container glass	Glass for insulating fibres

	Weight %						
Fe_2O_3	0.013	0.010	0.010	0.03	0.10	0.25	0.3
Cr_2O_3	0.00015	0.0002	0.0002	0.0005	-	-	-
Cu	0.0001	-	-	-	-	-	-
Co	0.0001	-	-	-	-	-	-
Ni	0.0001	-	-	-	-	-	-
V	0.0003	-	-	-	-	-	-

Table 23 The recommended chemical composition of glass-making sands.

The results showed that the % Fe_2O_3 present in the extracted sands was well below the recommendation for producing optical and ophthalmic glass. However, the % Cr_2O_3 detected in the extracted sand was too high for such use.

Further extractions and analysis of the sand are required to accurately determine the % Cr_2O_3, Cu, Co, Ni and V. Thus, to determine if the high purity sand could be used for the production of optical, ophthalmic, tableware, lead crystal or borosilicate glasses.

On an industrial scale the drawbacks to this technique are that 9 tonnes of KOH / tonne of cullet would be required. This technique also involves a number of filtration stages, which may be difficult when dealing with a large quantity of reagents.

4.3.2 Acid Washing

Approximately 4 g of ground cullet was added to 100 ml of acid (1:4). The samples were heated at 100 °C for approximately 4 hours. The samples were filtered and the filtrate was examined for % Fe_2O_3 and % Cr_2O_3. The residue was dried in an oven at 100°C for 1 hour.

4.3.2.1 Results

A semi-quantitative XRF analysis was carried out on the samples of green cullet that had been acid washed with HCl and HNO_3 acid for 4 hours. These results were compared to the XRF analysis of the untreated green cullet and are shown in Table 24.

	Green Cullet		
Analyte	**Untreated Sample (Weight %)**	**Treated with HCl ~ 4hrs (Weight %)**	**Treated with HNO3 ~ 4hrs (Weight %)**
SiO_2	69.96	73.26	72.91
Na_2O	14.33	11.89	11.83
CaO	11.15	10.47	10.71
MgO	1.21	1.19	1.20
Al_2O_3	1.92	1.85	1.90
K_2O	0.65	0.60	0.61
Cr_2O_3	0.27	0.26	0.29
Fe_2O_3	0.43	0.40	0.43
SrO	0.04	0.03	0.04
ZrO_2	0.04	0.05	0.05
MnO	-	-	0.04

Table 24 **A comparison of the semi-quantitative XRF analysis of the treated green cullet and the untreated sample.**

The analysis was carried out to indicate if any colorants were removed. However, it appeared that only a small % of Fe_2O_3 and Cr_2O_3 had been removed, if any at all. A low level wet chemical determination of the % Fe_2O_3 and % Cr_2O_3 was carried out on the HCl and HNO_3 filtrates. The results show that after 4 hours, 300 ppm Fe2O3 and 180 ppm Fe_2O_3 were removed from the green cullet using HCl and HNO_3 acid, respectively. Hence, HCl acid was more effective at removing Fe_2O_3 than HNO_3 acid. Table 25 shows the results obtained.

Green Cullet	Duration of experiment at 100°C	% Fe_2O_3 removed	% Cr_2O_3 removed
HCl	4 hrs	0.030	
HNO_3	4 hrs	0.018	0.0035
HCl	6 hrs	0.030	
HNO_3	6 hrs	0.018	0.0037

Table 25 **A Wet chemical determination of the % Fe_2O_3 and % Cr_2O_3 present in the filtrate after green cullet samples were boiled in acid (1:4) for the specified time period.**

The acid washing experiments were repeated using a time period of 6 hours with stirring throughout. The results obtained are shown in Table 25. Unfortunately, the wet chemical technique that was used to determine the % Cr_2O_3 could not be carried out on the filtrates containing HCl. Hence, the % Cr_2O_3 was only determined for the HNO_3 filtrates.

Although the experiment was repeated and carried out for 6 hours the same % Fe_2O_3 and % Cr_2O_3 was removed from the cullet as was observed for the 4 hour test. Hence, after 4 hours the maximum % Fe_2O_3 and % Cr_2O_3 was removed from the cullet. The experiments were repeated on the amber cullet, however, only the 4 hour test was carried out as after 4 hours the maximum % Fe_2O_3 was removed. The results are shown in Table 26.

Amber cullet heated at 100°C for 4 hours	% Fe_2O_3 removed
HCl	0.020
HNO_3	0.012

Table 26 **Wet chemical determination of the % Fe_2O_3 present in the filtrate after an amber cullet sample was heated at 100°C for approximately 4 hrs.**

The results show that 200 ppm Fe_2O_3 and 120 ppm Fe_2O_3 were removed from the amber cullet using HCl and HNO_3 acid, respectively. As was observed with the green cullet acid washing, HCl acid was more efficient at removing Fe_2O_3 than HNO_3 acid.

HCl and HNO_3 acid removed less % Fe_2O_3 from the amber cullet compared to the green cullet. However, this difference was negligible as only a very small percentage, 9 % and 7 % of the total Fe_2O_3 content was removed using HCl acid from the green and amber cullet, respectively.

4.3.2.1 Conclusion

Acid extraction only removed a very small percentage of the colorants from the cullet, as the contaminants were body bound and not surface discrete particles.

On an industrial scale this technique would be problematic as it would be very time consuming to grind cullet into small size fractions. It would also not be cost effective to use 25 m^3 of acid / per tonne of cullet to remove a low percentage of contaminants.

4.4 Alternative colouring system - Irradiation

Flint glass samples were melted from industrial batch materials and doped with the following levels of silver oxide:

Series Code	% AgO_2 Addition	% Flint Addition
IR1	0%	50%
IR2	0.03%	50%
IR3	0.30%	50%

Table 27 **Series of glasses for irradiation treatment with AgO_2 as a colour stabiliser, the series is as flint cullet additions to flint batch materials.**

The samples were polished and then colour measurement taken. After the initial colour measurements had been made, the samples were exposed to x-ray energy using an XRF (x-ray fluorescence) machine and placed in the path of an incident x-ray beam for 16 minutes. The x-ray excitation voltage varyied over the range 27 kV – 60 kV. The power output of the x-ray source remained approximately constant at 4kW. Colour measurements of the samples were then taken immediately after exposure to the radiation.

4.4.1 Results

The irradiated samples appeared to be amber in colour. CIE (a*b*L) colour coordinates were calculated and are shown below:

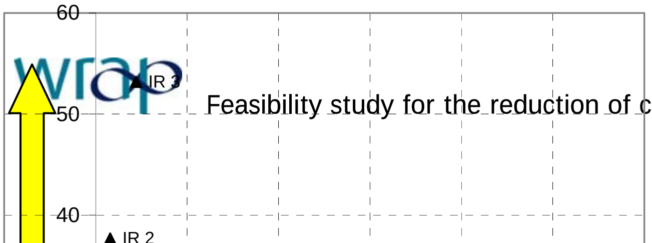


Figure 16 CIE colour space measurement for Ag_2O doped samples before (Blank) and after irradiation (IR1, IR2 & IR3).

The colour centre measurements (Figure 16) confirmed that the glass colour was in the yellow/red (brown) segment after irradiation. The results indicate that as the Ag_2O addition increased so does the intensity of the colour. As can be seen in Figure 17, the glass colour of sample IR3 appears slightly darker than the other samples, which is consistent with the levels of Ag_2O added to the glass matrix to stabilise the colour and to avoid colour fading with time. However, due to the length of the project it was not possible to report the rate of colour loss.

Potential further work would be to look at the change in colour of the irradiated samples over time, with a study into the effect of the various levels of silver and other oxide for stabilising colour.

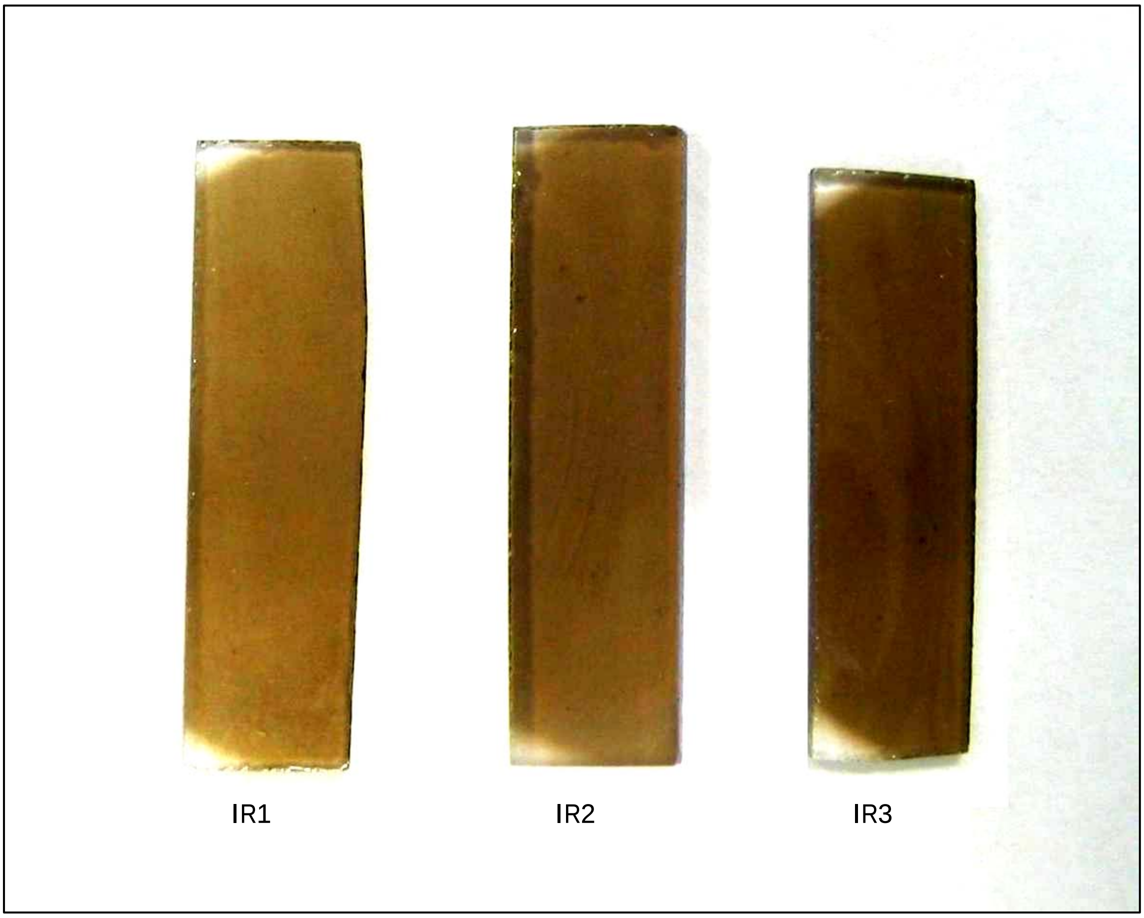


Figure 17 **Irradiated samples (IR1, IR2 & IR3).**

5 Summary & Conclusions

This work set out to review reported methods for reducing the colour of coloured container glass. Throughout this work the technicalities of the possible routes have been reviewed and appropriate observations made. The practicalities and economics of the possible routes were not fully investigated. However, where appropriate, comments have been made on the possible adoption of the investigated techniques.

The following is a summary of the techniques investigated.

5.1 Dilution, decolourising & colour balance

The use of coloured glass in flint melts is nothing new; in fact the level of coloured glass used in flint glass was once relatively high and glass makers were able to compensate with decolouriser additions. However, the amount of coloured glass in flint melts has reduced over recent years due to improvement in cullet processing with coloured glass removal equipment. Therefore, glass makers tend not to have the need to regularly modify the melt by using decolourising additions.

From the literature and the limited work undertaken there appears to be scope for investigating the use of a controlled addition of green and/or amber in flint melts. Currently the addition of green in flint is up to 0.5% in the final glass (<6000 tonnes/annum). At these levels the current decolourising addition is adequate. However, with further investigation it should be possible to increase the level of green in flint up to 2% or 3%. Based on current flint container glass production of approximately 1,200,000 tonnes/annum using a 40% cullet addition of which 3% is green cullet, then there could be a possibility of using 14,000 tonnes/annum. This could be further increased with higher cullet additions with slightly higher green cullet levels. With amber in flint it should be possible to increase further the addition, as amber tends to pull the colour away from green towards yellow/red.

Amber glass is far more tolerant of green cullet; up to 30% green cullet can be used in amber glass. Currently, amber glass production is only using approximately 20% cullet, this is primarily due to the lack of supply of amber cullet. Therefore, if amber glass production was capable of using 30% green cullet this could equate to approximately 75,000 tonnes/annum. However, the main consideration and limitation is the redox of the melt that needs to be controlled and monitored during melting.

This route has the potential to absorb controlled levels of mixed coloured glass, but further industrial research is required to fully understand the limitations. This would include the revisiting of different decolourising system such as Mn and Ni. One important consideration that was not investigated as part of this project is the consumer perception of slightly coloured glass containers. Market research needs to be undertaken to fully understand the impact of slightly coloured and/or loss of light transmission on the perception of glass containers as a suitable food or beverage container. Many containers produced in other European countries are significantly coloured.

5.2 Crystallisation and phase separation

It was not possible to undertake practical experiments for this route. However, the literature indicates that this route has the potential to produce relatively pure (>99%) compounds such as silica. However, there was only limited work undertaken and further research needs to be conducted.

5.3 Reductive melting

The reduction of Cr & Fe to form an alloy with silicon metal is technically feasible. However, the Cr & Fe in the metal inclusion was only from the surrounding glass due to the slow diffusion rate of Cr & Fe through the molten glass. Therefore, the overall Cr & Fe from the bulk glass was only slightly reduced. Also, the colour of the glass (green) was not reduced, in fact, due to the reducing conditions it appeared slightly darker in colour.

This route required the formation of metallic silicon, which is an inclusion that can cause catastrophic failure if embodied in the final glass container. Therefore, this route would not be appropriate as a method used in the glass melting furnace.

5.4 Electrochemistry

It was not possible to undertaken practical experiments within the scope of this project due to the complexity of the required equipment. The electrical extraction of metal ions from molten glass is theoretically possible. However, there are practical limitations such as suitable electrode materials and high temperature to reduce glass viscosity. This route has the potential to reduce the level of colorant ions in molten glass. However, there is only limited work undertaken in this technique and further research needs to be conducted to fully understand the feasibility of electrochemical extraction of colouring ions from molten glass.

5.5 Wet chemical extraction

The results of the alkali fusion route were very promising, producing relatively pure silica sand that could be used in glass making or other applications requiring finely ground high purity silica.

The acid washing approach only removed the Cr & Fe from the surface of the glass particle. Therefore, this route would not produce a suitable feedstock material for glass making.

The practicalities and economic of the alkali fusion route need to be investigated further before recommending it as a possible solution for removing Cr & Fe from green and amber cullet.

5.6 Alternative colouring system - Irradiation

The limited practical experiments indicated that it is possible to induce colour which was predominantly amber. Silver oxide was used to stabilise the colour, however, due to the short timeframe of this project it was not possible to determine how long the colour will be stable.

This route has the potential for manufacturers to melt only flint glass that is then coloured by irradiation. This would obviously have many implications on glass manufacturing and recycling. In addition, it would allow the manufacture to apply colour patterns to the glass container by masking certain areas. Therefore, further research needs to be conducted to validate this route as a commercially viable approach.

6 Recommendations

From the literature and practical work undertaken the following recommendations are made:

6.1 High Priority

6.1.1 Dilution, decolourising & colour balance

From an objective of increasing the use of recycled glass back into primary glass melting this route requires further investigation. With a scale up project initially undertaking large scale laboratory melts then moving to industrial trials. This would work as an industrial club project. The project should include the development of a computer model that would allow furnace managers to input the cullet level and colour composition and then determine decolouriser level.

6.2 Medium Priority

The following techniques are worthy of further investigation to understand the technical and economic implications. In the short term these routes will probably not direct any additional amounts of recycled glass back into glass melting but may have potential in the long term.

6.2.1 Irradiation

In-depth research and development project to fully investigate the technique of colouring glass by irradiation, with a commercial and marketing study on the viability of colouring flint glass by irradiation.

6.2.2 Crystallisation and Phase Separation

Research and development project to investigate the technique of crystallising desired phases out of coloured container glass.

6.2.3 Alkali Fusion (Wet chemical extraction)

Research and development project to fully investigate the technique of producing pure silica, including the identification of possible markets for the product.

6.3 Low Priority

Initial research indicated that the following techniques would have numerous complications including both practical and economic. Therefore, the following have been set aside as low priority for possible future investigation.

6.3.1 Electrochemistry

Research and development project to investigate the technique of preferentially extracting Cr & Fe by an electrochemical method.

6.3.2 Reductive Melting

Research and development project to investigate the technique of preferentially extracting Cr & Fe by a reductive melting method.