REPORT PREPARED BY ICER FOR DTI, AUGUST 2003

GW-12.10-130: NEW APPROACH TO CATHODE RAY TUBE (CRT) RECYCLING

Executive summary

The main barrier to recycling CRTs is the perceived lack of applications for glass which contains high levels of lead oxide and other undesirable metal oxides.

The objective of this project was to test two techniques – smelting and electrolysis - for removing metal oxides from waste CRT glass. The project was led by ICER. The experimental work was designed and carried out by Glass Technology Services.

The project also estimated arisings of waste CRTs in 2002, forecast arisings over the next 10 years and identified the environmental and legislative drivers for CRT recycling. In addition, it surveyed current approaches to CRT recycling in the UK.

Make up of CRTs

A CRT is composed of two different types of glass. One — used for the funnel and neck sections — is characterised by high levels of lead oxide and the other — used for the screen — is typically a non-leaded glass that contains high levels of barium oxide. There is considerable variation in the composition of glass, especially screen glass, made by different manufacturers.

In addition to glass, there are other materials in a CRT, including ferrous and non-ferrous metals, and coatings to the screen and funnel sections. CRTs are usually housed in a plastic casing.

Arisings of waste CRT glass

Arisings of waste CRTs in the UK in 2002 are estimated at 105,000 tonnes. This includes waste glass from TVs, PC monitors, monitors used in specialist applications and waste from the CRT assembly process.

Arisings of waste CRT glass from the same sources are forecasted to be 100,000 tonnes in 2012. This figure assumes a decline in waste glass from PC monitors because of the shift to flat screen display technology but an increase in glass from TVs because of larger screen sizes in later models. Waste CRTs from all sources except PC monitors are likely to continue to enter the waste stream for at least 25 years.

Drivers for CRT recycling

Environmental impact

Studies have shown that when CRTs are disposed of in landfill sites, lead can leach from the crushed glass and contaminate ground water. This is a major driver for CRT recycling. It is also important to reclaim the other materials, such as ferrous and non-ferrous metals and plastics, which are associated with CRTs.

Legislation

The WEEE (Waste Electrical and Electronic Equipment) Directive sets targets for material recycling and recovery of equipment containing CRTs. It is to be implemented in national regulations by 13 August 2004.

The European Waste Catalogue classifies CRTs as hazardous waste. This makes it more costly to dispose of CRTs under the Landfill Directive and also limits potential for exporting waste CRTs to non-OECD countries.

Barriers to CRT recycling

Mixed CRT glass (funnel, neck and screen glass) contains on average 5% lead oxide, 10% barium oxide and 2% strontium oxide. Waste glass of this composition is unsuitable for applications where metal oxides could leach into food products or ground water.

Survey of current approaches to CRT recycling in the UK

Currently in the UK, recycling of CRT glass is restricted to glass from the CRT assembly process and glass from some post-consumer PC monitors. This is because recycling of post-consumer CRT glass has a cost. The economic barriers to increased recycling of CRT glass are expected to decline when the WEEE Directive comes into force, requiring producers to pay the costs of recycling WEEE from households from August 2005.

Post-production waste CRT glass from the assembly process is mostly shipped to Europe for use in the manufacture of new CRTs. Some CRTs from end-of-life PC monitors are sent to a copper-lead smelter in Europe where the glass acts as a substitute for sand in the smelting process. Other CRT glass from monitors is used to make ceramic products. Little post-consumer CRT glass is sent for manufacture of new CRTs. This is because of the high cost of separating, sorting and processing the glass to meet the standards required by glass manufacturers.

Toxic metal removal

This project reviewed the possible technologies to extract the lead oxide and to a lesser extent barium and strontium oxide from the glass matrix, to render the glass non-toxic and suitable for use in other applications. Whole CRT units were crushed and used in the experimental work; this resulted in a mixed glass that contained approximately 5 weight % lead oxide, 10.8 weight % barium oxide and 2.4 weight % strontium oxide.

The two known technologies for extracting metal oxides from glass are:

- smelting to reduce the metal oxides to metal by melting the glass mixture in reducing conditions using reactants such as carbon or aluminium so that the metal forms into spheres and falls to the bottom of the glass melt
- electrolytic separation by applying a voltage across a molten bath of mixed glass so that the metal ions are attracted to the positive electrode and form metal from the oxide.

Findings

Experiments indicated that the glass smelting technique with the use of 0.5 weight % aluminium addition resulted in a glass with a 50% reduction of lead oxide from the mixed CRT waste, with metallic spheres of less than 1mm diameter suspended in the glass. In addition, the barium and strontium oxide were reduced by 30% and 35% respectively. Although the experiments showed that it was possible to reduce the lead oxide content in waste CRT glass by 50%, there was no indication that it would be possible to remove all the lead compounds from waste CRT glass.

The experiments also showed that electrolytic separation is not a practical technique for extracting metals from waste CRT glass. No measurable amounts of lead were removed from the glass structure during the course of the experiments.

However, the waste CRT glass used in both sets of experiments was coarsely crushed. If finely ground waste glass was used instead, it might be possible to further reduce the lead and metal oxide levels. This would involve additional cost.

Because of the residual lead, barium and strontium oxide content in the smelted waste CRT glass, this glass could not be used in applications where there are strict limits on permitted levels of these oxides, for example, in food and drink glass containers or water filtration media.

Recommendations

This work indicated that the removal of lead, barium and strontium oxide to an acceptably low level from mixed waste CRT glass was not practical under the experimental conditions investigated. It is therefore recommended that further work on waste CRT glass recycling should be directed at seeking suitable applications, either for mixed waste CRT glass or for lead oxide glass and barium oxide glass. However, if suitable and economic applications for waste CRT glass are not found, it is recommended that the approach of heavy metal oxide reduction be revisited.

1. Introduction

This project was led by ICER. The experimental work was designed and carried out by Glass Technology Services. The project was funded by the Department of Trade and Industry Recycling Programme.

The main barrier to recycling CRTs is the lack of applications and demand for glass which contains high levels of lead oxide and other undesirable metal oxides. The objective of this research project was to determine whether it is possible to remove lead and other metals from CRT glass to leave glass for which there would be market demand.

This project tested two techniques for removing undesirable metal oxides from glass:

- **Glass smelting** to reduce the metal oxides to metal by melting the glass with reactants such as carbon or aluminium. In this process metal oxides form into metallic spheres and fall to the bottom of the glass melt.
- **Electrolytic separation** where a voltage is applied across a molten bath of glass. In this process the metal ions are expected to be attracted to the positive electrode, forming metal from the oxide.

2. Approach

The project involved the following steps:

- Understanding the background to CRT recycling including:
  - — make up of CRTs
  - — current arisings of waste CRTs and future trends
  - — environmental impact of disposal
  - — legislative drivers for CRT recycling
- Surveying current approaches to CRT recycling in the UK
- Preparing for smelting and electrolysis trials
- Carrying out glass smelting work to separate out the metal oxides from the glass in CRTs
- Carrying out electrolysis work to separate out the metal oxides from the glass in CRT's
- Evaluating the potential for commercial application of the each of the processes under trial
- Evaluating the environmental impacts of both processes

3. Background to CRT recycling

3.1 Make up of CRTs

3.1.1 The glass

A CRT glass unit is composed of three different parts, each doing a different job and needing to be of a different glass composition. A typical structure is shown in Figure 1.

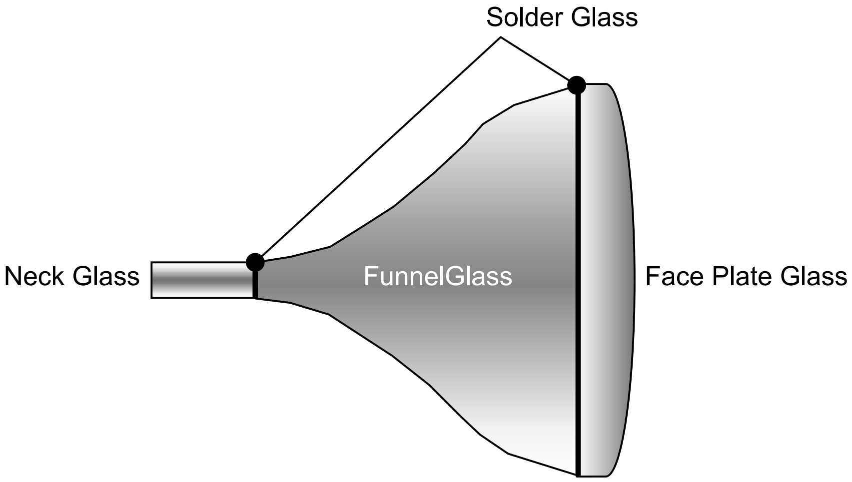

Figure 1. Main glass components of a typical CRT

The viewing section (known as screen, panel or face plate) is made of glass which typically contains a high level of barium oxide but no lead oxide (because this discolours glass under X-ray radiation). Both the funnel glass and the neck glass contain lead oxide to shield against X-ray radiation released by the high anode voltage. The funnel section contains up to 25% lead oxide. The neck section, housing the electron gun, has up to 40% lead oxide. The three glass components are joined together using a low melting temperature solder glass that also contains high levels of lead oxide (up to 60%).

Glasses made by different manufacturers will be of a different composition, especially the face plate glass. Analysis of compositional data derived from the GTS database and recent papers[1] shows the variations in glass compositions for the three components (Table 1, 2 and 3).

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[1] Glass for CRT tubes in TV sets and PC monitors, S. Hreglich & R. Falcone, International Glass Journal, 2000, No 107.

Oxide	Face 1	Face 2	Face 3	Face 4	Face 5	Average
SiO_2	62.55	64.6	61.52	67.36	63.26	**63.87**
Na_2O	7.86	7.87	8.86	7.92	7.81	**8.06**
K_2O	7.86	10.03	10.64	11.05	7.19	**9.35**
CaO	3.18	4.21	3.40		0.10	**2.18**
MgO	1.04	1.79	0.79	1.57		**1.04**
BaO	13.70	7.35	0.20	8.42	10.30	**7.99**
SrO			10.45		9.00	**3.89**
Al_2O_3	3.58	3.43	3.86	3.68	1.77	**3.26**
TiO_2		0.42			0.57	**0.20**
CeO_2	0.23	0.30	0.28			**0.16**

Table 1. Five typical faceplate glass compositions

Oxide	Fun. 1	Fun. 2	Fun. 3	Fun. 4	Fun. 5	Average
SiO_2	58.96	49.97	67.95	57.99	55.15	**58.00**
Na_2O	7.76	5.92	6.93	8.24	6.32	**7.03**
K_2O	8.40	10.08	7.20	8.83	8.36	**8.57**
CaO	5.30	3.65	0.34	5.34	3.57	**3.64**
MgO	2.83	3.70		2.83	1.53	**2.18**
BaO	0.80	1.98	12.45	1.31	0.81	**3.47**
PbO	11.38	20.22		10.85	22.43	**12.99**
Al_2O_3	4.57	4.48	5.13	4.61	1.83	**4.12**

Table 2. Five typical funnel glass compositions

Oxide	Neck 1	Neck 2	Neck 3	Neck 4	Neck 5	Average
SiO_2	47.40	58.62	58.91	58.22	44.80	**53.59**
Na_2O	2.18	3.52	3.65	3.75	2.00	**3.02**
K_2O	10.92	12.93	11.90	12.78	16.50	**13.01**
CaO	2.10	1.57	1.15	1.70	0.10	**1.32**
MgO		0.81	0.82	0.99		**0.52**
BaO		6.29	6.31	6.93	0.70	**4.05**
PbO	34.30	12.77	12.74	11.91	35.00	**21.34**
Al_2O_3	3.10	2.14	1.74	2.31	0.90	**2.04**
B_2O_3		1.35	2.78	1.41		**1.11**

Table 3. Five typical neck glass compositions

The main environmental concern about CRT glass is the amount of lead oxide and, to a lesser extent, the barium and strontium oxides it contains. The other major constituents of CRT glass are silicon (60%), sodium (10%), potassium (8%), aluminium (2%) and calcium (1%) oxides. These are relatively inert and need not be removed from the glass to render it suitable for other applications. In fact, these oxides are common constituents of most commercial glasses such as container glass and flat glass.

Figure 2 shows the least desirable metals (or its oxide form) in order. The composition of the waste CRT glass contains lead, strontium, barium, calcium, magnesium, cerium and aluminium; all in the oxide form.

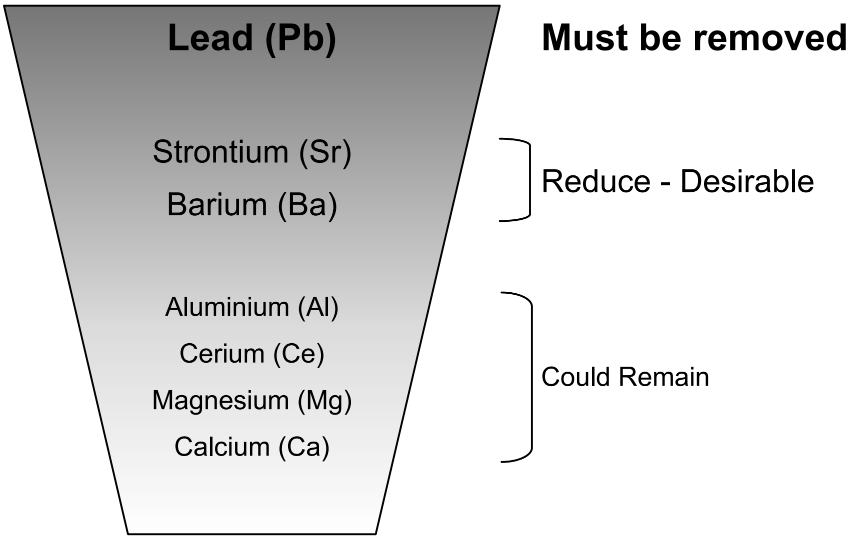

Figure 2. Ascending order of desirability of metals in processed waste CRT glass

3.1.2 Other materials

The inside of the screen of a CRT is coated with a mixture of phosphors which may also contain cadmium and other heavy metals especially in older equipment. Inside the screen there is a metal mask (the shadow mask). The funnel section has an outer coating of graphite and an inner coating of iron oxide. Around the welded section between the flat and the conical sections of the CRT there is a steel anti-implosion band. The cylindrical extension of the funnel, also called the neck, houses the gun which fires electrons at the screen. This consists of a series of metal electrodes placed inside the glass cylinder with electrical connections extending through, and sealed by, the glass. The whole assembly is subjected to a high vacuum. Placed around the gun and the narrow end of the conical section is a copper deflector coil held in place with adhesive.

The CRT is usually housed in a plastic casing but older TVs may have metal or even wood surrounds. The plastic is likely to contain halogenated flame retardants and other fillers, including cadmium-based stabilisers, and in some instances may be sprayed with a metallic coating on the inside, or have a metal screen affixed to the inner surface as an aid to lowering electromagnetic emissions from the product. There is also electronic circuitry within the casing.

3.2 Arisings of waste CRT glass

3.2.1 Sources of waste CRT glass

There are three sources of post-consumer waste CRT glass:

- TVs
- PC monitors
- monitors for specialist applications such as cash dispensers, industrial control, and graphic design

There is also waste from the production process — both assembly of CRTs and glass manufacturing. For this research, only waste from the assembly process has been counted towards total arisings of CRT glass. This is because waste from the glass manufacturing process is normally recycled into the next batch as it is of known purity and composition. It therefore does not count towards total arisings of waste CRT glass.

3.2.2 Arisings of waste CRT glass 2002

3.2.2.1 Arisings of waste CRT glass from TVs

Arisings of TVs in 2002 were calculated using manufacturers' sales data for 2002 and data on the national stock of TVs in the UK. The national stock is defined as the number of TVs (including non-working sets) in UK households and commercial establishments, e.g. hotels and offices. Data from manufacturers[2] suggest that there was no significant change in the national stock of TVs in 2002. Therefore, the number of TVs disposed of in 2002 can be assumed to equal the number of TVs sold, i.e. 5.8 million units[3]. These sales figures include all TVs containing a CRT, regardless of whether they were for domestic use or for use in commercial settings such as hotels and offices.

However, the quantity of glass in TVs disposed of in 2002 will depend on the age of those TVs. The average weight of glass in a TV has increased by some 30% over the last 12 years as screen

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[2] Philips Electronics

[3] Philips Electronics

sizes have increased. Also, the introduction of the flat screen technology has required more glass thickness to counteract the strength reduction due to the loss of the inherent strength from the curved screen. In 1990 the average weight of glass in a TV was estimated 11.8 kgs per unit, rising to 15.6 kgs per TV by 2002[4].

Estimates for the average life of TVs range from eight-and-a-half to 14 years[5] and market research has shown that people do not in general dispose of a set while it is still working. Even when they buy a new model they continue to keep working sets, either in another room or in storage[6]. This research assumes that TVs have an average life of 12 years. Therefore, the estimated weight of glass in TVs disposed of in 2002 will equal the weight of glass in TVs manufactured around 1990. This can be estimated at 69,000 tonnes.[7] However, not all TVs disposed of actually enter the waste stream. A small number are repaired for re-use in the UK and, in addition, up to 10,000 units a week are thought to be exported for re-use abroad[8].

3.2.2.2 Arisings of waste CRT glass from PC monitors

Arisings of waste CRT glass from PCs monitors in 2002 were calculated using data on average life and sales data from the appropriate year.

The estimated average first life of a PC monitor is five years. This is based on manufacturers' market research and is corroborated by data from recyclers and refurbishers who handle IT equipment, including monitors. Unlike TVs, most PC monitors are disposed of while still working. This is because they are largely owned by businesses and are therefore written down and replaced after a certain period, whether or not they are working.

Arisings of waste CRT glass from PC monitors disposed of in 2002 are estimated at 26,000 tonnes. This figure equals the weight of glass in PC monitors sold in 1997, and assumes that a monitor contains the same weight of glass as a TV of the same size[9] [10].

Because many of the PC monitors disposed of in 2002 were still in working order, it is estimated that about 15% were re-used within the UK and a further 30% were exported for re-use abroad, including countries outside the EU. However, the re-use of monitors in the UK is not expected to have reduced the amount of glass available for recycling because in addition to models sold in 1997 older monitors that had already been re-used would finally be entering the waste stream. Now that CRTs have been classified as hazardous waste by the European Waste Catalogue, the practice of exporting used monitors outside the EU may well be stopped under the Basel Convention which bans the export of hazardous waste to non-OECD countries. This will depend, however, on whether used monitors are defined as waste.

3.2.2.3 Arisings of waste CRT glass from specialist applications

There are no data for arisings of waste CRT glass from monitors used in specialist applications. Arisings are estimated at 5,000 tonnes per annum.

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[4] Philips Electronics

[5] GfK and Philips Electronics

[6] Survey of householders, Comet and Domestic & General, 1998

[7] Philips Electronics

[8] Reclaimed Appliances

[9] Brian Norris Associates

[10] Philips Electronics

3.2.2.4 Arisings of waste CRT glass from the production process

There are no waste arisings from the two CRT glass manufacturing plants in the UK. The manufacturing process results in approximately 20% production waste but because this is of known composition and purity it can be recycled into the next batch.

There are three CRT assembly operations in the UK, although one will be closing at the end of 2003. Waste arisings from the assembly process include reject components and breakages and are estimated to amount to between 1,000 and 5,000 tonnes a year.

Source of waste	**Tonnes glass**
TVs	69,000
PCs	26,000
Specialist applications	5,000
Assembly waste	5,000
Total	**105,000**

Table 4. Arisings of waste CRT glass 2002

3.2.3 Future trends for arisings of waste CRT glass

3.2.3.1 TV disposals 2003 to 2012

There were an estimated 65 million TV sets in the UK at the end of 2002. Household penetration of TV sets was at 2.23 sets per household in 2002, accounting for some 57 million sets[11], and an estimated further 8 million are owned by hotels and other commercial operations.

Assuming the average weight of glass per TV set is 13.7 kgs (the mean between the average of weights of glass in TV sets in 1990 and 2002), the estimated total weight of glass in these 65 million sets is 890,500 tonnes. All of this will ultimately end up in the waste stream and much of it is likely to become waste within the next 15 years.

To forecast arisings of CRT glass from waste TVs over the next 10 years the following assumptions were made.

- Colour TVs are normally disposed of only when they cease to work. This is based on anecdotal evidence from individual TV manufacturers, market researchers GfK and trade association Intellect (which includes TV manufacturers).
- The average life of a TV set is 12 years, although estimates range from eight-and-a-half years[12] to 14 years[13] and TVs older than 20 years have been found in practical collection trials.
- Sales of TVs have averaged five million per annum over the last 12 years and have ranged between four and six million per annum[14].

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[11] GfK, 2003

[12] GfK, 2003

[13] Philips Electronics, 2003

- The sales profile of TVs has changed over the last 12 years such that the weight of glass in TVs sold in 2002 is some 30% greater than for the number of TVs sold in 1990.

From 2003 to 2012, waste CRT glass will arise from TVs sold before 2002. Although the number of units disposed of is predicted to be constant at around five million units per annum, the weight of glass in those units will increase over time, reflecting the changes in profile of TVs sold. In 2003, therefore, arisings of CRT glass are estimated at 70,000 tonnes (based on 1991 sales), rising to some 90,000 tonnes in 2012 (based on 2000 sales).

3.2.3.2 TV disposals 2012 to 2025

It is likely that TVs containing CRTs will continue to enter the waste stream for at least 25 years. This is because sales of such TVs are predicted to continue for at least the next 10 years[15] and are likely to last a further eight to 14 years before entering the waste stream. Sales of CRT-containing TVs are expected to continue, despite the introduction of digital TVs and flat screen technology[16]. This is partly because of the higher cost of new technology but also because of the durability and the high picture quality of CRT TVs.

Technical advances in TV manufacture and programme transmission are thought unlikely to affect the rate of disposal of CRTs in the short term. Most TVs containing CRTs are expected to enter the waste stream only when they cease to work and. arisings are therefore expected to peak around 2014 to reflect what is thought to be a peak in sales of CRT-containing TVs some 12 years earlier. Arisings are then expected to begin to decline but still be significant for a further 10 years.

3.2.3.3 PC monitors

Arisings of waste CRT glass from PC monitors are expected to peak in 2005. This is because sales peaked in 2000[17] and PC monitors are assumed to have an average life of five years. Arisings of CRT glass from PC monitors are expected to be negligible by 2014. This is because of the shift towards flat panel display technology.

3.2.3.4 Specialist applications

There are no data on projected arisings of CRT glass from monitors used in specialist applications. Arisings have therefore been assumed at a constant 5,000 tonnes per annum, 2002 to 2014.

3.2.3.5 Production waste

Arisings of waste CRT glass from the assembly process are expected to decline over the next 10 to 12 years. This is partly because CRT production itself is expected to decline and also because CRT glass manufacturing is expected to move outside the EU. By 2014 production waste is estimated at a maximum of 2,000 tonnes per annum from assembly in the UK.

Source of waste	Tonnes glass
TVs	91,000

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[14] British Radio and Electrical Manufacturers Association Annual Report 2000
[15] Schott and Philips Electronics, 2003
[16] Philips Electronics, 2003
[17] Brian Norris Associates 2003

PCs	2,000
Specialist applications	5,000
Assembly waste	2,000
Total	**100,000**

Table 5. Projected arisings of waste CRT glass 2014

4. Environmental impact of CRT disposal

4.1 Environmental impact of disposing of CRTs to landfill

CRTs can cause environmental problems when disposed to landfill, in particular the leaching of lead and other heavy metals into ground water. Work carried out by Corning in the early 1990's[18] looked at the leaching of lead metal from CRT materials. This work showed that both time and temperature would affect the rate of extraction. The work made predictions that up to 13% of the lead could be extracted from the glass matrix. The study also found that increasing the surface area, by reducing the particle size, resulted in increased levels of extraction of lead. The risk of lead ions leaching from CRT glass is estimated to be increased one thousand fold when the glass is crushed in landfill sites. This has significant implications for using crushed CRT glass in road aggregate.

Little work has been done to look at the possible leaching of barium from crushed CRT glass.

4.1.1 Loss of resource from disposing of CRTs to landfill

Because of the perceived lack of applications for waste CRT glass there is no economic incentive to dismantle monitors and TVs to recover the other materials found in them such as ferrous and non-ferrous metal and plastics. This will change, however, with the implementation of the WEEE Directive that makes producers responsible for the costs of recycling equipment containing CRTs.

4.2 Barriers to recycling CRTs

Mixed CRT glass (funnel glass, neck glass and screen glass) contains on average 5% lead oxide, 10% barium oxide and 2% strontium oxide. Waste glass containing these amounts of metal oxides is unsuitable for applications where the oxides could leach into food products or ground water. Lead glass from CRTs is unsuitable for container glass applications — the Packaging Waste Regulations limit the amount of lead, cadmium, mercury & chromium VI allowed in container glass to 200 ppm. However, this limit might be reduced to 100 ppm by 2006.

If CRTs are split to separate the lead oxide glass from the barium oxide glass, this gives higher concentrations of lead in the lead oxide fraction but increases recycling options for the barium oxide fraction. However, there are concerns about the toxicity of barium which could limit its use.

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[18] Lead Extraction from CRT Glasses, D.E. Goforth, L.R. Morse, S.T. Gulati, Corning Research, 1994, p74-76.

5. Legislative drivers for CRT recycling

5.1 The WEEE Directive

The WEEE (Waste Electrical and Electronic Equipment) Directive requiring recovery and recycling of a wide range of electronic and electrical equipment was published in the Official Journal and became European Law on 13 February 2003. Member states must have in place national regulations to implement the directive within 18 months of the date of publication in the Official Journal i.e. by 13 August 2004.

5.1.2 How the directive relates to CRTs

CRTs are contained in two types of equipment covered by the scope of the directive — computer monitors (Category 3: IT and Telecommunications Equipment) and televisions (Category 4: Consumer Equipment). For equipment containing CRTs, the recycling target is 65% and the recovery target 75%. This means that 65% of the total material and/or components must be recycled and/or re-used. A further 10% of the material must be recovered by processes such as incineration with energy recovery.

These recovery and recycling targets apply to the whole piece of equipment containing a CRT, not the CRT itself. Since CRTs are thought to account for between 40% and 50% of the weight of monitors and televisions, meeting the targets will require some element of the CRT to be recycled. Exactly how much will depend on how much of the rest of the piece of equipment is recyclable.

CRTs are also listed in Annexe 2 as one of the components of WEEE which have to be removed before recycling and recovery can take place. The phosphor coatings have to be removed.

5.2 European Hazardous Waste Catalogue

Changes in the European Waste Catalogue came into effect in January 2001. As a result, CRTs are now classified as hazardous waste unless they arise from domestic households. This will affect the way waste CRTs can be transported, stored and disposed of.

5.3 The Landfill Directive

The landfill regulations for England and Wales came into force in June 2001 to implement the Landfill Directive. Equipment classed as hazardous by the European Waste Catalogue must now go to specially designated hazardous waste landfill sites. This affects TVs and computer monitors from commercial operations and may at some stage also affect arisings from private households. The Landfill Directive is likely to lead to increased disposal costs for CRTs, particularly if after July 2004 there is a shortage of hazardous waste landfill sites when the current practice of co-disposing of hazardous and non-hazardous waste must end.

6. Survey of current approaches to CRT recycling in the UK

In the UK, CRT recycling is restricted to production waste from the CRT assembly process and post-consumer PC monitors. Glass from the assembly process has a positive value and can be sold to CRT glass manufacturers when sorted, separated and cleaned as required. Post-consumer CRT glass, however, currently has no value and there is a cost associated with recycling. Some commercial end-users are prepared to pay for PC monitors to be recycled, but local authorities, which handle most waste TVs, are unable to pay for recycling. This is why

CRT recycling is currently restricted to PC monitors. The economics are unlikely to change until the WEEE Directive comes into force and requires producers to pay for recycling from August 2005.

6.1 Applications for post-production waste CRT glass

6.1.1 Use in manufacture of new CRTs

Waste glass from the production process — of known composition and purity — can be used as feedstock for new CRTs. However, if the barium oxide and lead oxide glass is mixed, the potential for use in new CRTs is limited. Because of its lead oxide content, mixed glass can only be used in the manufacture of funnels and amounts are limited because the quantity of lead oxide is diluted in mixed glass. It is not possible to use mixed glass in screen manufacture because screens cannot contain even small amounts of lead oxide since this will discolour the glass under X-radiation.

In order to maximise the use of waste CRT glass in new CRTs, the tubes have to be split apart in a way which guarantees there is no lead attached to the screen glass. Recent developments in screen splitting have overcome many of the technical barriers to this but there is still a cost involved for separating the glass and removing other contaminants such as electronics, coatings and corner pin.

Separation of CRTs is a well-established route for post production waste i.e. rejects from the assembly process. The separated glass is cleaned and mostly shipped to continental Europe for further processing and use in the manufacture of new CRT components. All funnel glass is shipped to Europe for re-use since funnel glass is not manufactured in the UK. There are two facilities which manufacture screen glass in the UK and some of the UK's production waste is re-used to make new screens in this country, although amounts are limited. This is because each facility manufactures screens to a particular colour specification and it is difficult to incorporate glass of unknown composition from different manufacturers.

6.2 Applications for post-consumer CRT glass

6.2.1 Use as flux in smelting

Some CRTs from PC monitors are sent to a smelter in Belgium which treats copper and lead-bearing metallic scrap. The CRT glass acts as a substitute for sand in the smelting process and ends up in the slag which can then be used as road aggregate. The CRTs are manually removed from the plastic casing and ventilated before being introduced into the furnace.

The quantity of CRTs that can be used to replace sand in this way is limited partly by the type and design of furnace and the way that it is charged and partly by limits on the levels of certain substances, e.g. barium oxide and lead oxide, in the resulting slag if this is to be used as aggregate.

The only types of smelter that can use CRT glass are those which use sand, can tolerate lead and are designed in such a way that CRT glass can be incorporated. Research so far indicates are that there are three smelters in Europe currently prepared to accept CRT glass and that the volumes of glass that can be taken are far below the amount of waste generated just in the UK, let alone in the whole of the EU. Further work needs to be done to quantify the potential demand for CRT glass in this application across the EU.

6.2.2 Use in ceramics and building products

One electronics recycling company in the UK is processing CRT glass for use in the ceramics industry. To be used in this way the glass must be free from contamination and ground to a sand-like consistency[19]. There could be potential for greater use of CRT glass in the ceramics and building products industry, either to manufacture bricks and tiles or as a flux in brick and ceramic manufacture. Further work is required to identify any technical barriers and assess the economic viability of this approach.

6.2.3 Use in manufacture of new CRTs

Some CRT glass manufacturers now accept post-consumer CRT glass as feedstock for the manufacture of new CRTs. However, because the manufacturing process for new CRT glass is very sensitive to contamination, the use of post-consumer waste CRT glass varies from manufacturer to manufacturer and continues to be low.

This research found only one manufacturer prepared to use post-consumer screen glass in the manufacture of new screens. Use in funnel glass manufacture is more common but only one manufacturer uses more than 10% and some manufacturers do not use any at all.

Little UK post-consumer glass currently goes for manufacture of new CRTs. This is largely because of the costs of splitting the tube and processing the glass to meet the stringent quality standards for feedstock demanded by glass manufacturers.

Post consumer CRT glass has to be rigorously pre-processed to remove all contamination from other materials before it can be incorporated into the manufacturing process. Feedstock, particularly for screen manufacture, must be of high standard because the colour and quality of the screen are vital and any flaw at all is unacceptable.

Further work is required to establish total potential capacity across the EU for the use of post-consumer CRT glass in new CRTs.

6.3 Application in development for CRT glass

6.3.1 Specialist smelting to remove lead

Development work has been carried out in the UK to smelt CRT glass in the presence of a catalyst to remove the lead from the glass leaving an alkali silicate which can be used in the manufacture of new glass. This process is not yet in commercial operation and there is no published data on the process or its results.

7. Preparing for smelting and electrolysis trials

It was decided that the smelting and electrolysis trials would be carried out using mixed CRT glass, i.e. a mixture of neck, funnel and screen glass in the proportions in which they arise.

7.1 Compositional analysis of CRT sample

The material composition of the CRT glass used in the smelting and electrolysis trials is shown in Table 6.

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[19] Bruce Electronics, 2003

Component	% Composition
Faceplate	40.24
Silvered funnel glass	30.50
Mixed unidentifiable glass	26.40
Glass & paper	1.77
Metals	0.75
Bonded plastic	0.35

Table 6. Material composition of CRTs used in trials

The composition of the glass fraction of the CRTs used in the trials was determined by melting samples and undertaking chemical analysis. The results of this are shown in Table 7.

Oxide	Wt%
SiO_2	60.92
BaO	10.80
Na_2O	8.96
K_2O	7.44
PbO	5.02
SrO	2.39
Al_2O_3	2.07
CaO	0.67
ZrO_2	0.43

Oxide	Wt%
Sb_2O_3	0.33
F	0.30
CeO_2	0.16
Fe_2O_3	0.15
MgO	0.14
TiO_2	0.11
ZnO	0.10
CuO	0.01

Table 7. Chemical composition of CRT glass used in smelting and electrolysis trials

7.2 Mechanical processing of sample

The CRT glass used in the smelting and electrolysis trials was crushed to a particle size of between 50 and 5 mm. The trials were conducted using mixed CRT glass.

8. Glass smelting work

8.1 Overview

The aim of the glass smelting work was to free metals from their oxide state present in the glass matrix. This process, an adaptation of traditional smelting technology, leaves the burden (glass melt) as the required material. The addition of reducing agents to the glass produces metal from the metal oxides in molten glass. The reducing nature of the glass produced means that the free metal will not reform as oxides and will remain as molten metal spheres within the body of the glass. Adding sodium oxide may reduce the density and viscosity of the melt promoting segregation of the metallic inclusions by allowing the separated metal spheres to descend to the bottom of the melt in a shorter period.

8.2 Technical background

Previous work by GTS has shown that the addition of carbon to melts of waste CRT glass, fluxed with sodium carbonate will lead to the production of the metallic form of certain elements, in particular lead.

Fluxing waste CRT glass with sodium carbonate reduces the viscosity of the melt allowing the metals to 'drop out' of the melt under reducing conditions. The metal particles formed by the reduction of the oxide to metal, are expected to drop to the base of the melting vessel, as they are denser than the molten glass. Different alloys may be removed at different rates depending on their density. Table 8 shows the time calculated for a 1 mm diameter sphere of different metals to move a distance of 100 mm in molten glass at 1400°C. The viscosity of glass at the melting temperature is approximately 10 Pa.s, as a comparison the viscosity of water at room temperature is 0.001 Pa.s

Metal Inclusion	**Density (g/cm^3)**	**Time (seconds)**
Lead	11.34	200
Copper	8.89	400
Barium	3.78	1450
Aluminium	2.69	9250
Strontium	2.58	22950

Table 8. Time for various metal inclusions to descend 100 mm, under gravity, in molten glass at 1400°C

8.2.1 Thermodynamics

The reduction of an oxide to a metal is driven by thermodynamic reactions. The speed and the effectiveness of these reactions is affected by:

- The presence of a primary reducing addition such as carbon or metallic aluminium.
- The presence of secondary carbon in the melt from plastic contamination and the use of a carbon crucible for melting. This increases the level of carbon available for the reduction reaction.
- The presence of sodium oxide in the melt. This will lead to increased availability of oxygen making the reducing process slightly harder. However, the sodium oxide lowers the glass viscosity, hence, increasing the mobility of metal particles in the melt and allowing them to fall.

8.2.2 Extraction of metals from the oxide

The reduction of oxides into elemental components relies on the interaction of the oxide with an element that has a greater affinity for the oxygen than the element present in the oxide.

The use of carbon at 1400°C for the reduction of metals such as lead, iron, copper and chromium from waste CRT glass is thermodynamically feasible. However, the more reactive elements such as strontium and barium will require a reducing agent with greater reactivity, of which aluminium metal is the most suitable.

Increasing the reactivity of the reducing agent will also increase the probability of silicon metal being extracted from the melt. An increase in the processing temperature will allow the reduction of a greater amount of the transition elements, but may also lead to the reduction of SiO_2 to metallic silicon. SiO_2 is a majority constituent of glass (known as a glass former) and it is, therefore, undesirable to reduce the level of this oxide in the glass melt.

It is not necessary to remove calcium, magnesium and aluminium from the melt; as these elements are typical glass constituents within the glass matrix and have relatively low toxicity.

8.2.3 Other considerations

The use of a neutral atmosphere during processing, such as nitrogen or argon, may be advantageous, as it will prevent the premature oxidation of the reducing agents before reactions occur.

After processing, bubbling oxygen through the melt may be useful: this will encourage the oxidation of residual carbon that would otherwise contaminate the glass. It is unlikely that this process will re-oxidise the reduced metals as they would have dropped to the base of the crucible and not be exposed to the oxygen. The metals are also likely to have formed agglomerates of alloys and diffusion of oxygen through these particles will be relatively slow.

8.3 Smelting process

The figure 3 shows the process route used for the smelting trial.

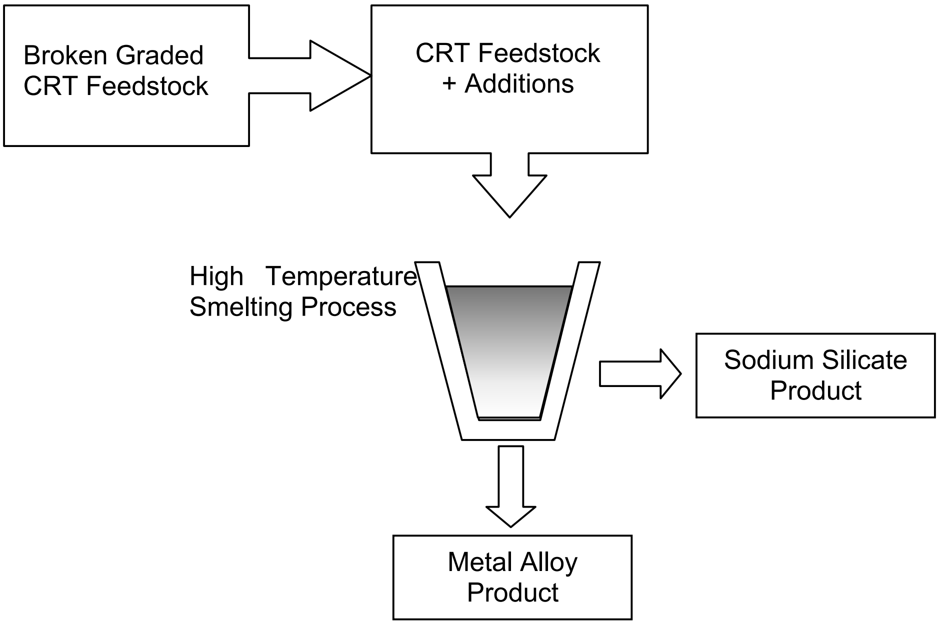

Figure 3. Process route used for the smelting trials

8.3.1 Process evaluation

The process evaluation involved an experimental programme to look at the operational parameters of a smelting treatment unit. The programme investigated the burden composition, furnace operating temperature and processing time.

8.3.2 Furnace design

GTS designed the melting facility in-house. In order to operate at a scale that was practical, the design load of the furnace was approximately 8 kgs of molten materials. The furnace was designed to operate at a maximum temperature of 1450°C and to take crushed mixed CRT glass.

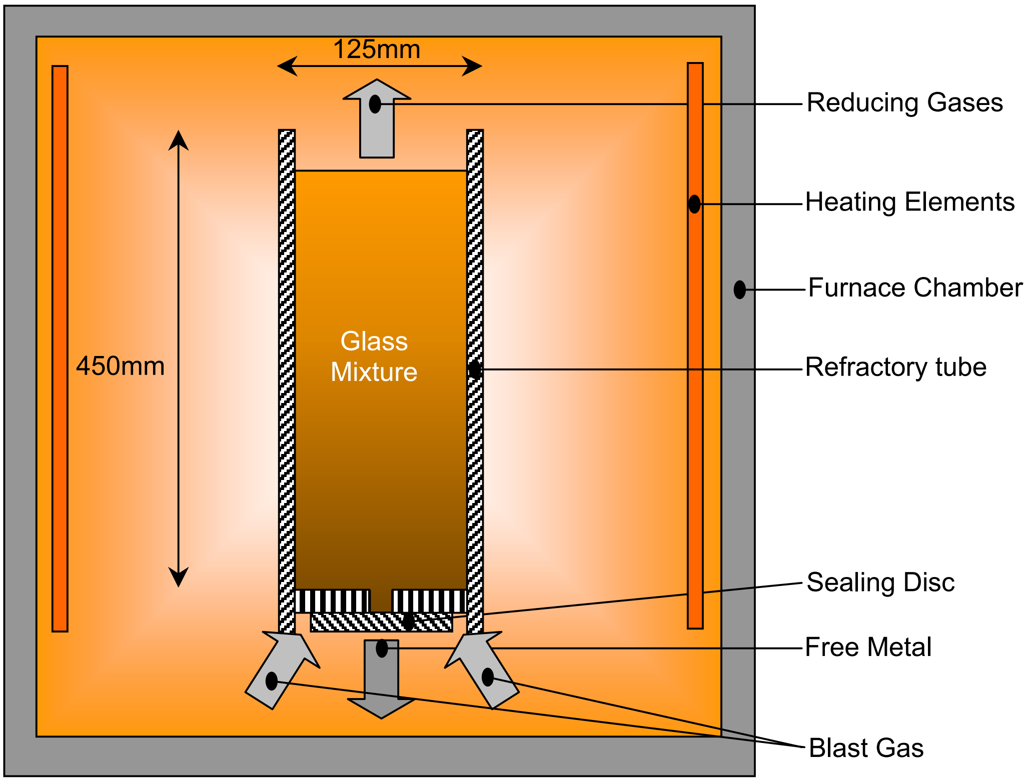

Figure 4. The smelting furnace experimental set-up

A crucible was assembled from a refractory tube and a refractory disc with a drain hole (Figure 4 and Figure 5). Another disc was used to seal the hole during the smelting trial. The purpose of the drain hole was to allow glass to be removed during the course of the melting trial. There were holes in the bottom disc to allow blast gas to be passed into the melt, if deemed necessary. The whole assembly was heated in an electric furnace using vertically installed heating elements, allowing controlled heating and cooling of the furnace, in conjunction with electronic controllers built to operate the heating chamber. Although electrical heating may not be chosen for commercial operation, it was used for the smelting trial because it was cleaner and more controllable than gas-firing in the laboratory stages of the experiments.

8.3.3 Smelting trials

Two reducing agents were identified through the literature search: carbon and aluminium metal. Two series of glass melts were therefore conducted to investigate the efficacy of these reducing agents. The operating temperature and the amount of reducing agent used were varied in each series. The batches were weighed and mixed with a representative sample of glass from the stockpile.

Figure 5. Cross section of the refractory tube used in the smelting trials

8.3.3.1 Carbon addition smelting trials

Table 9 shows the parameters for the carbon addition smelting trials. The graphite powder was a finely ground source of carbon, whilst the anthracite powder was a courser source of carbon (particle size between 2 and 4 mm).

Sample ID	Reduction Agent Addition	Operating Temperature	Reducing Agent
GC.0	None Added	1200°C	
GC.1	5.00 wt%	1200°C	Graphite powder
GC.2	2.50 wt%	1200°C	Graphite powder
GC.3	1.00 wt%	1200°C	Anthracite powder
GC.4	1.00 wt%	1200°C	Graphite powder
GC.5	1.00 wt%	1300°C	Graphite powder
GC.6	1.00 wt%	1400°C	Graphite powder
GC.7	0.50 wt%	1400°C	Graphite powder
GC.8	0.25 wt%	1400°C	Graphite powder

Table 9. Series 1 - Carbon melting trials.

The work with carbon additions investigated the level of carbon addition, the burden composition and the furnace operating temperature. The time of the melt was two hours for all of the carbon trials.

8.3.3.2 Results of melting trials on waste CRT glass and carbon

GC.0 This melt had no carbon addition, therefore, no metal reduction was observed. The glass had reasonable homogeneity but contained some non-reacted metals; copper wire and corner pins still remaining in the melt at 1200°C. The glass was a blue purple colour.

GC.1 This generated a grey coloured, opaque material. Examination under an optical microscope revealed this to be a mixture of metallic materials and non-reacted carbon powder trapped in the glass. The reduced metal was suspended as spheres in the glass melt. This was due to the high viscosity of the molten glass, therefore, the metal spheres could not fall to the bottom of the melt within the time of the experiment. Due to the dispersion of the metal throughout the melt, it was not possible to determine the level of metal removed.

GC.2 Reducing the level of carbon addition did little to prevent the presence of non-reacted carbon powder trapped in the glass. The trials at 1200°C implied that the carbon was not reducing metals in the glass as required. Metallic spheres were left suspended in the melt, as in GC.1. It was therefore not possible to determine the amount of metal reduced.

Figure 6. Sample GC.1.

GC.3 In order to try and reduce the level of carbon remaining in the glass, the reducing agent was added as anthracite (coarser particle size). This seemed to react more with the glass, lessening the grey colour caused by incorporation of carbon. There were still, however, significant metallic inclusions in the molten glass and it was not possible to determine the level of metal reduced.

GC.4 The graphite powder addition was further reduced and this resulted in a similar level of reduced metal as seen in GC.2. Again, the viscosity did not allow the metallic spheres to fall to the bottom of the melts and making it impossible to determine the level of metal removed.

GC.5 The temperature was increased by 100°C. There was no evidence of metallic spheres falling to the bottom of the melt. Again it was not possible to determine the level of metal removed.

GC.6 The temperature was increased by a further 100°C. There appeared to be some larger metallic spheres in the melt, evidence that the reduced metals were accumulating to form larger spheres. However, the metallic spheres were not of sufficient size or mass to counteract the glass viscosity. Therefore, they remained as suspended metal spheres in the melt and it was not possible to determine the level of metal removed.

GC.7 The graphite powder addition was further reduced. There appeared to be more metallic spheres than GC.6. The colour of the glass was a lighter grey than GC.6, due to less carbon particles remaining in the melt. Again, the metallic spheres were not of sufficient size or mass to counteract the glass viscosity. Therefore, they remained suspended in the melt and it was not possible to determine the level of metal removed.

Figure 7. Sample GC.7, with finely dispersed metallic particles (not visible on the photograph) in the glass

GC.8 The graphite powder addition was further reduced. There appeared to be a similar number of metallic spheres as GC.7. However, the colour of the glass was a slightly lighter grey. Again, the metallic spheres were not of sufficient size or mass to counteract the glass viscosity. Therefore, they remained suspended in the melt and it was not possible to determine the level of metal removed.

8.3.3.3 Aluminium addition smelting trials

Table 10 shows the parameters for the aluminium addition smelting trials. The powder was a finely ground source of aluminium whilst the granular aluminium was a courser source of aluminium, with a particle size between 5 and 8 mm.

Sample ID	Reduction Agent Addition	Operating Temperature	Reducing Agent
GA.0	None Added	1200°C	
GA.1	5.00 wt%	1200°C	Aluminium powder
GA.2	1.00 wt%	1200°C	Aluminium powder
GA.3	0.50 wt%	1200°C	Aluminium powder
GA.4	0.25 wt%	1200°C	Aluminium powder
GA.5	0.50 wt%	1300°C	Aluminium powder
GA.6	0.50 wt%	1400°C	Aluminium powder
GA.7	0.50 wt%	1400°C	Granular aluminium

Table 10. Series 2 - Aluminium melting trials on waste CRT glass

The work with aluminium additions followed the same strategy as that for the smelting work with carbon additions, varying the level of addition and furnace operating temperature and investigating the resulting burden composition. As with the carbon melts the melt period was two hours.

8.3.3.4 Results of series 2 aluminium melting trials on waste CRT glass

GA.0 This melt had no aluminium addition, therefore, no metal reduction was observed. As with GC.0, the melt produced a glass with reasonable homogeneity, but contained some evidence of incomplete melting at 1200°C. The glass that was uncontaminated had a blue purple colour throughout the body of the glass.

GA.1 The addition of finely divided powder had caused reduction of the glass itself, forming grey coloured opaque material. Examination under an optical microscope revealed this to be a mixture of metallic spheres. There was less evidence of non-reacted aluminium powder trapped in the glass. This may be because the aluminium metal oxidised during melting and became part of the glass as an oxide. Due to the high viscosity of the molten glass, the metal spheres could not fall to the bottom of the melt within the time of the experiment. Due to the dispersion of the metal throughout the melt, it was not possible to determine the level of metal removed.

GA.2 Reducing the level of aluminium addition started to prevent the reduction of the glass itself. At 1200°C the aluminium seemed to be reducing the metals from the glass as required but there was still a tendency at this level of aluminium addition for the silica in the glass to be reduced to metallic silicon. This is a recognised phenomenon in glass making and in order to reduce this, the level of addition was decreased below 0.5% (GA.3) for the higher temperature trials. Metallic spheres were suspended in the melt, same as GA.1, therefore, not possible to determine the metal removed.

GA.3 Reducing the level of aluminium further seemed to increase the reaction with the glass, producing a grey coloured glass and a number of metallic spheres of diameter greater than 1mm suspended in the glass.

GA.4 The aluminium powder addition was further reduced, and this resulted in a similar amount of reduced metal as in GA.3. There was evidence that silicon spheres were present in the glass melt. The viscosity did not allow the metallic spheres to fall to the bottom of the melts and therefore not possible to determine the level of metal removed. Compositional analysis of the bulk glass showed 4% PbO, 8.2% BaO and 1.6% SrO after the melt.

GA.5 The temperature was increased by 100°C. Some slightly larger metallic spheres suggested that agglomeration was taking place. However, no metallic spheres fell to the bottom of the melt. Again it was not possible to determine the level of metal removed. Compositional analysis of the bulk glass showed 3.9% PbO, 7.9% BaO and 1.5% SrO after the melt.

GA.6 The temperature was increased by a 100°C. There appeared to be more and larger metallic spheres in the melt showing that the reduced metals were agglomerating to form larger spheres, some of which were falling to the bottom of the melt (Figure 8). However, the majority of the metallic spheres were not of sufficient size or mass to counteract the glass viscosity. Therefore, most remained as suspended metal spheres in the melt and it was not possible to determine the level of metal removed. Compositional analysis of the bulk glass showed 3.3% PbO, 7.9% BaO and 1.5% SrO after the melt.

Figure 8. Initial melt, sample GA.6

Figure 9. Initial melt, sample GA.6 showing metallic particles at the bottom of the melt

GA.7 The additional of granular aluminium was less effective, principally due to the larger size leading to surface oxidation of the metal. This protective coating of oxide prevented the further reaction of the metallic aluminium with the glass matrix.

8.3.3.5 Remelt trial to reduce lead

In order to explore the melting work further, the glass, which had been melted at 1400°C with 0.5% (GA.6) of powdered aluminium metal, was remelted. The aim was to determine if re-melting with a new reducing agent would cause further reduction in the lead content.

The glass was sorted and any metallic inclusions removed from the burden. The furnace was recharged and a further 0.5 weight % aluminium metal and remelted at 1400°C for two hours, the optimum cycle from the GA melts.

There appeared to be no noticeable metallic inclusions at the bottom of the melt or within the body of the melt. Chemical analysis confirmed that there had been no significant further reduction of metals from the glass matrix.

8.3.4 Product evaluation

The glass resulting from the Series 1 carbon melts was not analysed because it could be seen that it would not be suitable for use in alternative products. This was due to the residual carbon and the finely divided metal spheres in the glass.

The glass from the Series 2 aluminium melts was, however, analysed and evaluated. It appeared to be of a satisfactory quality. The resulting metallic material, present in spheres up to 4 mm diameter, was also analysed.

8.3.4.1 Analysis of metal resulting from aluminium addition smelting

The chemical analysis of the metallic materials taken from the GA.6 melt showed that they were either an alloy of lead, barium and strontium or rich lead particles.

8.3.4.2 Analysis of glass resulting from aluminium addition smelting

The smelting of CRT glass with 0.5 weight % addition of aluminium metal (GA.6) produced the largest amount of free metal. The glass was extracted from the bottom of the furnace during the melt and compositional analysis of the glass was undertaken at intervals during the melt. The lead oxide content of the glass had been reduced by approximately 50% by weight, down to 3 % lead oxide after 90 minutes.

8.4 Conclusion

The presence of carbon in the melt did not provide a practical method of reducing out the metals from the waste CRT glass. The more reactive elements, such as strontium and barium, were shown to require a reducing agent with greater reactivity. Higher additions of carbon led to more free carbon in the glass matrix and there was little evidence of significant volumes of metal being formed during melting. Changing the size and type of carbon addition did not bring about any major improvement in the process.

The addition of aluminium to the glass melt at levels above 2.5% resulted in increased reactivity but reduced the silica (silicon oxide) to silicon metal, There were also non-reacted materials in the glass. Dropping the level of aluminium metal below 0.5 weight % proved more effective.

Chemical analysis of the metallic inclusions confirmed that a majority contained lead metal either with other metals such as barium and strontium or as mainly lead metal.

After 90 minutes the lead oxide content of the glass had been reduced by approximately 50% by weight, down to 3% lead oxide. After this time the level of lead in the glass appeared to increase again, up to 4 weight %. This may have been due to the oxidation of the metals back to oxides, a phenomenon which could be promoted by the reduction in the amount of reducing materials in the melt as the aluminium was oxidised.

In all the trials conducted there was no significant quantity of metallic material at the bottom of the melt as would be expected. This was due to the convection current in the glass, and the high viscosity of the glass for keeping the metal in suspension. If this process were developed into a commercial process the design furnace would need to be reconsidered to minimise the convection currents and hence allow small metallic particles to fall to the bottom of the melt.

The remelting of GA.6 with 0.5 weight % aluminium powder indicated that no further metals could be extracted from the melt. From this it can be concluded that 50% reduction of the lead oxide content was the practical limit with this process.

8.4.1 Summary comments

- Metal reduction did occur from the glass matrix when exposed to carbon or aluminium powders at melting temperatures (1400°C).
- Aluminium powder was more effective than carbon at reducing the heavy metals, especially the lead from the glass matrix.
- Aluminium additions below 0.5% brought about a 50% reduction of the lead content of the waste CRT glass.
- For all of the glasses melted during the smelting trials, the minimum level of lead oxide in the glass produced was 3% by weight in the glass.
- The reduction process led to the generation of a large number of small metallic spheres throughout the molten glass.
- Without a mechanism to agglomerate into larger spheres, the metal was held in suspension in the glass.
- Optimum reaction times were short, less than two hours for the removal process to take place.
- Further melting did not increase the lead reduction from the glass matrix; 50% was maximum reduction of lead oxide from the series of experiments conducted.

9. Electrolytic separation work

9.1 Overview

Electrolysis is the process whereby metals and some gases can be removed from a solution by the application of an electrical potential. The objective of this work was to investigate the feasibility of using the electrolysis process to remove metals from a molten glass bath. The proposed system would employ a DC current and, by varying the applied electrical potential, it was hoped that metals could be removed from the glass in a selective manner.

9.2 Literature survey

Electric melting of glass has been carried out since the early 1900s. For simple melting purposes the usual practice is to employ an AC rather than a DC supply as the continual reversal of the current inhibits the electrolysis process that would cause free metals and oxygen to be liberated at the electrodes. Therefore, the use of DC would allow the migration of metal ions to an electrode.

9.3 Electrolysis of Glass

Molten glass contains positive and negative ions which can be extracted by the electrolysis process. The metal ions within the glass carry a charge and are attracted to an electrode (cathode). Each metal has a characteristic charge; typically the more reactive metals carry a higher charge. The differences in charges carried by the various metals should, in theory, allow for selective removal of the metals by varying the electrode potential. In practice the process is somewhat more complicated and the order in which metals are removed from the body of molten glass is influenced by several factors including: time, the magnitude of the current, the operating temperature, the concentration of solution, the physical size of the electrodes and the geometry of the system itself. A further consideration is the viscosity of the glass. The migration of ions to the electrode will be inhibited by a viscous liquid. As a general principle the viscosity of a liquid falls with increasing temperature.

9.4 Electrical Resistance of Glass

At ambient temperatures glass is considered to be a good electrical insulator. Heating the glass reduces its insulating properties. At a temperature of approximately 700°C most glasses have lost their insulating properties. At higher temperatures the electrical resistance of the glass is inversely proportional to temperature i.e. higher the temperature, the lower the electrical resistance.

The variation of electrical resistance with temperature has been studied for some common (soda-lime) glasses. However there appears to be no data on the electrical characteristics of CRT glass and certainly none exist for the glass composed of mixed CRT glass waste. There is however some information on a glass of a similar composition to the mixed CRT glass waste used in this work and this data was used to predict the electrical resistance of the waste CRT glass used in this work.

Table 11 shows the temperature and electrical resistivity data of this "similar" glass upon which subsequent calculations were based.

Temperature (°C)	Resistance (ohm)	Resistivity (ohm.cm)
1250	28.5	38
1300	22.5	30
1350	17.25	23
1400	12.75	17
1450	9.75	13
1500	7.50	10
1550	6.75	9

Table 11. Variation of electrical resistance and resistivity with temperature for a similar glass composition to the mixed CRT glass waste used in this work. Resistivity is the reciprocal of specific electrical conductivity.

9.5 Electrolytic separation process

The figure below shows the process route for the electrolysis trials.

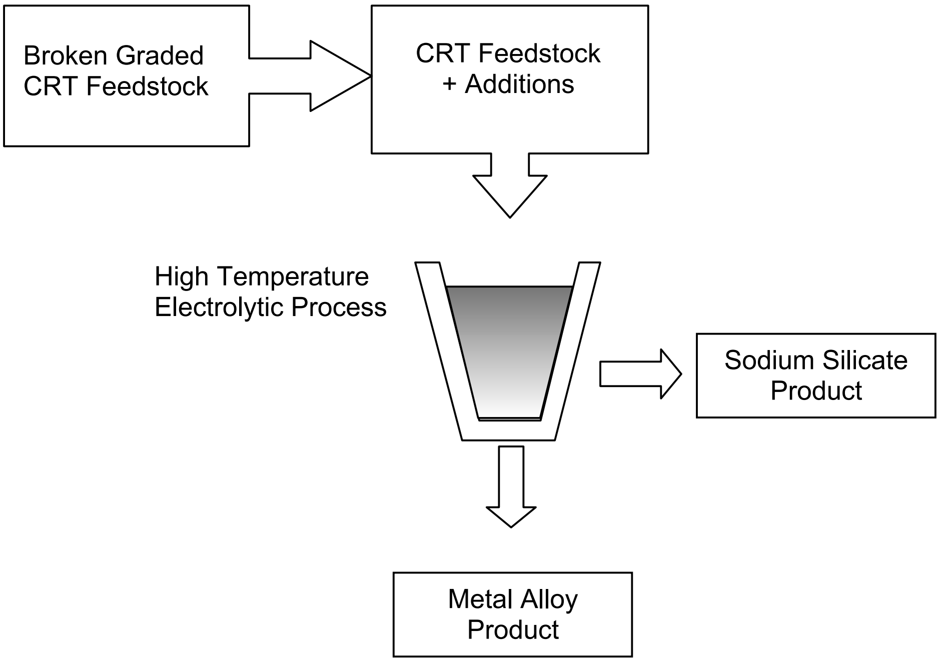

Figure 10. Process route used for the electrolytic trials

9.5.1 Process evaluation

The process evaluation involved an experimental programme looking at the operational parameters of an electrolytic treatment unit. The programme investigated the burden composition, furnace-operating temperature, processing parameter and processing time.

9.5.2 Furnace design

GTS designed the melting facility in-house. In order to operate at a scale that was practical, the design load of the furnace was approximately 4.5 kgs of molten materials. The maximum design temperature for the furnace was 1450°C.

9.5.2.1 Furnace construction and operation

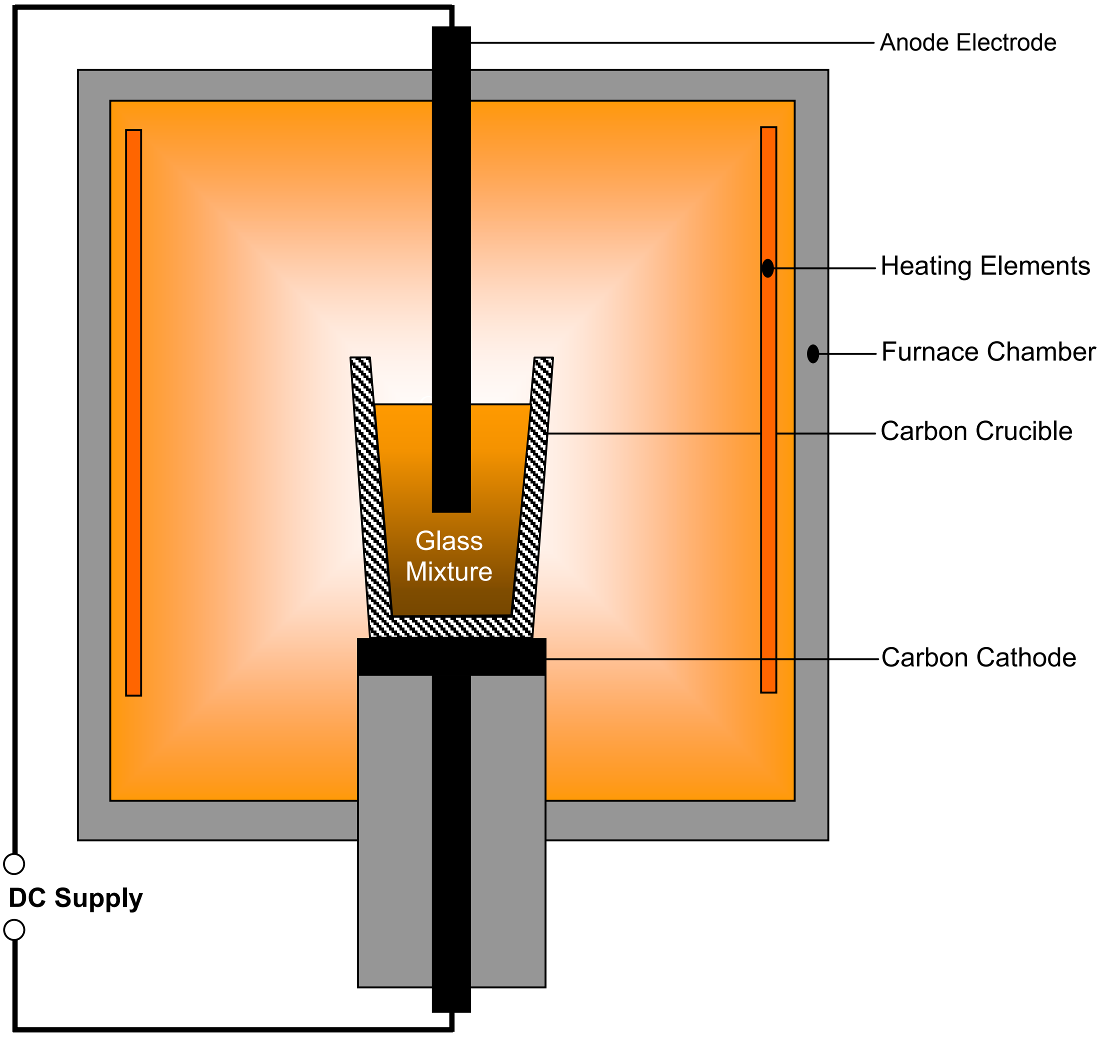

Figure 11. The experimental set-up for the electrolytic melting trials

A carbon crucible was mounted on a carbon plinth, with an electrode in the glass melt to complete the electrical circuit. The whole assembly was heated in an electric furnace using vertically installed elements. These allowed the controlled heating and cooling of the furnace in conjunction with the electronic controllers built to operate the heating chamber. While electrical heating may not form part of the final furnace design, it was cleaner and more controllable than gas-firing in the laboratory stages of the experiments.

9.6 Electrolytic trials

A series of glass melts were designed to investigate operating temperature, electrode material and processing parameters. The batches were weighed and mixed with a random sample of glass from the stockpile. The trials were conducted on 4.5 kg melt as detailed in Table 12.

Sample I	**Voltage Applied (volts)**	**Current Measured (amps)**	**Operating Temperature**	**Electrode Material**
GE.0	120	1.5	1200°C	Carbon
GE.1	120	2.9	1200°C	Carbon
GE.2	120	3.6	1300°C	Carbon
GE.3	120	3.2	1400°C	Carbon
GE.4	150	4.6	1400°C	Molybdenum
GE.5	180	4.5	1400°C	Titanium

Table 12. Electrolytic melting trials

9.6.1 Results

GE.0 The glass was not able to conduct any significant current. Examination of the crucible did reveal the presence of free metal in the base, as well as erosion of the electrode in contact with the glass. There were some metallic spheres at the interface between the glass and the carbon crucible.

GE.1 Again the glass was not able to conduct any significant current. And again, examination of the crucible did reveal the presence of free metal in the base, as well as erosion of the electrode in contact with the glass. There were some metallic spheres at the interface between the glass and the carbon crucible.

GE.2 Increasing the operating temperature for a similar voltage did generate slightly higher currents. However, there was also evidence of reaction at the central electrode, which confirmed that the gasses liberated from the melt were preventing the electrical contact between the glass and the electrode. While this is also the case for electrolysis experiments conducted in aqueous solutions, the viscous nature of glass prevents these gases from rising to the surface. In addition, the carbon electrode was being oxidised as it reached the higher temperatures attained above the melt. There was no free metal in the melt except at the interface between the crucible and glass due to oxide reduction, as demonstrated in the smelting trials.

GE.3 Increasing the operating temperature for a similar voltage did generate slightly higher currents. However, the experimental observations were the same as GE.2.

GE.4 Molybdenum metal was used as the electrode material; this is commonly employed in the glass industry as an electrode for glass melting and electrical boosting. This test showed that initially a slightly higher current was passed into the glass, but this tended to fall off over time. Observations of the surface of the melt seem to show less vigorous reaction at the surface compared to the carbon electrode. The molybdenum also suffered from oxidation above the surface of the melt and severe erosion occurred at the flux line. However, there was no free metal in the melt except at the interface between the crucible and glass due to oxide reduction.

GE.5 Titanium metal was used as the electrode material; it has good high temperature properties and electrical conductivity. Titanium metal also shows oxidation above 600°C but this occurs less rapidly than molybdenum. This trial had a very similar outcome to GE.4, with the passage of a limited current, reaction at the electrode / glass interface and free metal in the base of the crucible.

9.7 Conclusion

These trials demonstrated that there are many practical difficulties with this method for metal (lead) extraction from waste CRT glass. In none of the trials was there any evidence of metal separation in the glass melt. The only separation was at the crucible and glass interface, which was due to oxide reduction due to the presence of carbon. Therefore, this approach is neither economic nor practical for treatment of waste CRT glass.

9.7.1 Summary comments

- Theoretical study of the oxides present suggested that it was possible to extract metals from molten glass.
- Melting at higher temperatures did little to increase the metal removal from the glass.
- Reactions at the electrode prevented the passage of any significant currents.
- The electrolysis route proved to be of limited interest due to the practical problems involved and limited effects seen.

10. Potential for commercial application

There is no potential for commercial application for either of these techniques using the approach applied in this research. This is because it was not possible to remove sufficient lead from the glass, either by smelting or by electrolysis, to make it suitable for use in other applications.

11. Environmental impact of smelting

Both the techniques investigated for the reduction of metal oxides from mixed waste CRT glass required a relatively large input of energy. A detailed review of the environmental impact and risk of the techniques investigated has not been undertaken because there is no potential for commercial application.

12. Conclusions

The practical experiments showed that the glass smelting technique with the use of 0.5 weight % aluminium addition, resulted in a glass with a 50% reduction of lead oxide from the mixed CRT waste, with sub 1mm diameter metallic spheres suspended in the glass. In addition, the barium and strontium oxides were reduced by 30% and 35% respectively. Using this approach it does not appear to remove all or even the greater part of lead compounds from waste CRT glass.

The waste CRT glass used in this work was coarsely crushed. If further processing were undertaken using finely ground glass it might be possible to further reduce the lead and other heavy metal oxide levels. However, this would introduce a further processing cost and it is unlikely that the lead content would be sufficiently reduced to enable the glass to be used in other applications.

The trial of electrolytic separation carried out in this research showed that this is not a practical technique for the extraction of metals, in particular lead, from waste CRT glass. No measurable lead removed from the glass structure during the course of the experiments.

13. Recommendations

This work indicated that the removal of lead, barium and strontium oxide to an acceptably low level from mixed waste CRT glass was not practical under the experimental conditions investigated. It is therefore recommended that further work on waste CRT glass recycling should be directed at seeking suitable applications, either for mixed waste CRT glass or for lead oxide glass and barium oxide glass. However, if suitable and economic applications for waste CRT glass are not found, it is recommended that the approach of heavy metal oxide reduction be revisited.