

**Raija Siikamäki**

# Glass Can Be Recycled Forever

Utilisation of End-of-Life Cathode Ray Tube Glasses  
in Ceramic and Glass Industry





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# Summary

The aim of this study was to find possible applications, in which glass materials from End-of-Life (EOL) Cathode Ray Tubes (CRT) can be utilised in ceramic and glass industry. The qualitative objective of the study was to find utilisation targets and applications, where the properties of EOL CRT glass material can be as beneficial as possible.

This study is based on experimental work, which was first carried out on laboratory scale. The applications that gave promising results were tested on an industrial scale. In the ceramic industry, use as a raw material in glaze for low-fired and for high-fired products were found possible for CRT glass utilisation and further studied. In glass industry, test series were performed in hollow-ware glass production with four different production techniques (blowing, centrifugal casting, conventional casting and kiln casting) and production of construction blocks with sintering method. The tests covered both use as a raw material for the glass body of construction blocks and use as a coating material for blocks made out of container glass.

The results for these industrial application areas show that EOL CRT colour panel glass is a suitable raw material for ceramic glazes, both for low-fired and high-fired ceramics. Glazes for low firing area with firing temperature of 1020°C utilised up to 95 wt-% CRT panel glass. Glazes for high firing area with firing temperature 1260°C had CRT glass as a theoretical substitute for feldspar in glaze oxide composition. The properties of glazes containing up to 14.5 wt-% of CRT glass were found to be similar to commercial glaze.

In glass industry, melting tests were performed with 100% recycled CRT colour PC panel glass and formed with different production techniques: blowing, casting and centrifugal casting. The material performed well both in melting and forming

processes. The quality of formed products was found to be good, too. The products were tested for chemical durability by washing tests (500 and 1000 washings) and leaching tests without any failure. Construction blocks containing 95 wt-% of CRT glass were formed out of material grinded to particle sizes ranging from 0.1 to 10 mm. Formed blocks were sintered and finished by polishing the surface. By changing the proportions of various particle sizes, variations in grey colour hue typical to CRT panel glass were obtained.

The use of recycled material brings along many environmental benefits in high-temperature applications: it saves raw materials, but it also allows lower temperatures for melting glass or for firing ceramics, thereby reducing energy consumption. The use of recycled glass, a material that has already once been processed, reduces emissions to air from a glass melt or from a ceramic firing. Additionally, utilisation of EOL CRT glass in ceramic and glass industry makes a continuous recycling chain possible: the products, in which recycled material is used, are also recyclable. However, the possible disadvantages are contaminations recycled materials can bring along.

Experimental work for this study was carried out at the University of Art and Design Helsinki, Department of Ceramics and Glass, during a European Union's Brite/Euram project RECYTUBE 1997–1998 and during a Finnish national KIMOKELA project 2001–2003, financed by National Technology Agency of Finland. Laboratory-scale experiments and tests were carried out at the University of Art and Design Helsinki, while industrial-scale tests were done in Finnish ceramic and glass industries.

# List of original publications

**This thesis is based on the following papers, which will later be referred to by their Roman numerals:**

## **I**

Raija Siikamäki, Eckart Döring, Jorma Manninen, Closed-loop and Open-loop Applications for End-of-Life Cathode Ray Tube Glass Recycling, Proceedings of “Going Green, CARE Innovation 2002”, Vienna, 2002

## **II**

R. Siikamäki, L. Hupa, Utilisation of EOL CRT-Glass as a Glaze Raw Material, Recycling and Reuse of Glass Cullet, ed. Ravinda K. Dhir, Mukesh C. Limbachiya, Thomas D. Dyer Thomas Telford Publishing, London, 2001

## **III**

R Siikamäki, End-of-Life Cathode Ray Tube Glass as a Raw Material for Hollow Ware Glass Products, Recycling and Reuse of Waste Materials, ed. Ravinda K. Dhir, Moray D Newlands, Judith E Halliday, Thomas Telford Publishing, London, 2003

## **IV**

R Siikamäki, Glaze for Low-Fired Ceramics from End-of-Life Cathode Ray Tube Glass, Glass Waste, ed. Mukesh C. Limbachiya and John J. Roberts, Thomas Telford Publishing, London, 2004

## **V**

Raija Siikamäki, Jätteestä tuotteiksi – TV- ja tietokonelaitteiden monitorilasin hyödyntäminen, Kestävää muotoilua. Ympäristömyötäisyys tuotesuunnittelussa, Susan Vihma (toim.), Työpaperit, Taideteollisen korkeakoulun julkaisusarja, F 24, Helsinki, 2002

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## Part II

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**II** R. SIIKAMÄKI, L. HUPA,  
Utilisation of EOL CRT-Glass as a Glaze Raw Material

**III** R. SIIKAMÄKI  
End-of-Life Cathode Ray Tube Glass as a Raw Material  
for Hollow Ware Glass Products

**IV** R. SIIKAMÄKI  
Glaze for Low-Fired Ceramics from End-of-Life Cathode Ray Tube Glass

**V** RAIJA SIIKAMÄKI  
Jätteestä tuotteiksi – TV- ja tietokonelaitteiden monitorilasin hyödyntäminen



# Part I

Raija Siikamäki



# 1. Background

Consumption of Electric and Electronic Equipment (EEE) increases constantly. Besides that the number of the electronic devices increases, their lifetime becomes shorter as new models with more advanced capacities replace the old ones at an ever quicker pace. Today, the number of PCs in use worldwide amounts to about 575 million (Forrester Research 2004). The number of TV-sets currently in use is estimated to be 2 milliard (Kopacek 2002). The growing amount of the devices reaching their end-of-life stage raises the question on how to handle this waste stream in an environmentally and economically sound manner.

## 1.1. Material Product Lifecycle

Product lifecycle can be presented on the different aspects. The conceptual product life-cycle refers to the product as a concept starting from idea and via research and development, production, introduction to market, market penetration and becoming outdated finally is substituted by a different product. The material product lifecycle refers to a product as a physical object. The material product lifecycle is a set of sequences of processes in a product's life: the main steps are production, consumption and waste processing. Steps in the production process, shown in Figure 1, include production phase subdivided into three subsequent steps: material production, parts production and assembly. After consumption and possible repair, products are dismantled, separated and discharged. The linear product process chain can contain three different steps of re-use: re-use as a product, parts re-use and material recycling. When materials are considered, waste is generated in the production process, i.e. process waste. Some of the materials become waste at the end of the product's lifecycle. It is important that recycling processes favour re-use in all its forms. (Lambert 2001, Stead and Stead 1992, McDonough and Braungart 2002)

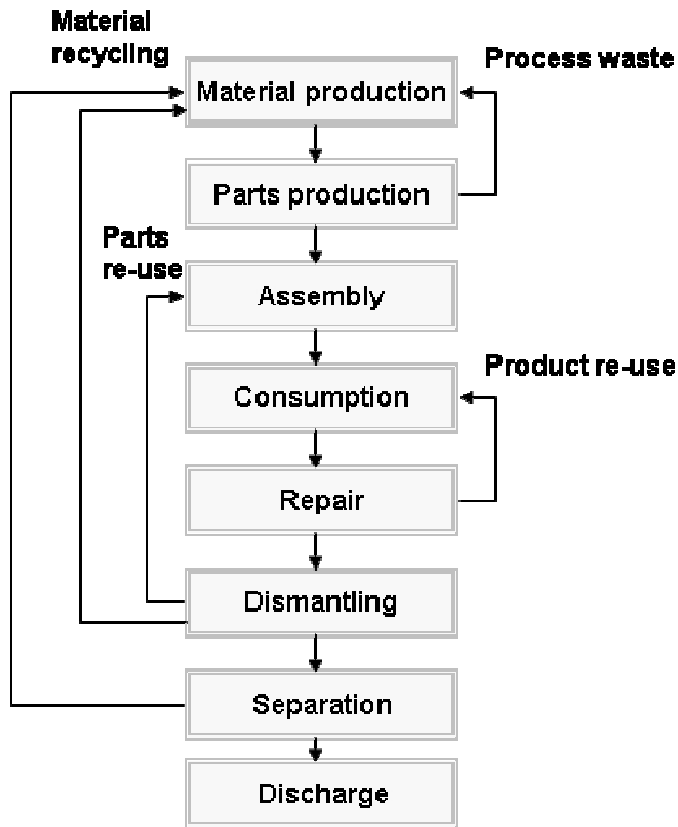


Figure 1. Product process chain for complex products (adapted from Lambert 2001).

Recycling of complex products, such as EEE, poses many different challenges. Reverse logistics have been defined by “Seven Rights” as following: ensuring the availability of the right product, in the right quantity and the right condition, at the right place, at the right time, for the right end-user, at the right cost” as cited by Martin (2001). In terms of devices containing Cathode Ray Tubes, there are several material flows, such as glass, plastics and metals, coming from recycling process. Each material flow has to be led to its own path of “Seven rights”.

## 1.2. Waste of Electric and Electronic Equipment

The waste stream of electrical and electronic equipment has been identified as one of the fastest growing waste streams in the European Union. To prevent this material flow to be wasted, the WEEE (Waste Electrical and Electronic Equipment) Directive of European Communities classifies discarded electrical and electronic equipment containing components, such as Cathode Ray Tubes containing lead, as waste that cannot be landfilled. Further, according to the directive, the re-use and recycling of material and substances has to be at least 65 % by an average weight per appliance. As a consequence, the industry faces new challenges in the re-use of End-Of-Life (EOL) Cathode Ray Tubes (CRTs). The waste stream of EEE has been estimated to constitute 4% of the municipal waste. The amount of WEEE is going to increase by 16–28% every five years, which means a growth three times as fast as that of average municipal waste (European Commission 2000).

The estimated total amount of EOL CRT glass originating in Western Europe in year 2003 was 280 000 tons. Estimates are based on an average lifetime of 8 years for PCs and 12 years for TV appliances. The average total amount of glass material per device is 3.8 kg in a PC and 11.0 kg in a TV (Guy-Schmidt and Thamin 1998). In the future, the growing popularity of plasma and Liquid Crystal Display (LCD) monitors will bring about a decline in the waste from CRTs. However, waste cathode ray tubes are likely to continue to enter the recycling market still for one to two decades.

Waste of electronics and electrical devices is typically heterogeneous and complex for their materials composition: it contains both organic and inorganic substances in many forms. The recycling process of devices containing a CRT includes separation of different materials in many phases. In a possible process flow to generate raw materials from End-of-Life TV and PC devices, shown in Figure 2, plastics and metals are removed from glass parts in the dismantling phase. This is followed by cleaning functional layers from glass parts. Separated glass fractions are then crushed and screened. After this they can be utilised after as raw material to the same production where it originated, i.e. to closed-loop recycling or to new products, in which case the material is re-used in open-loop application.

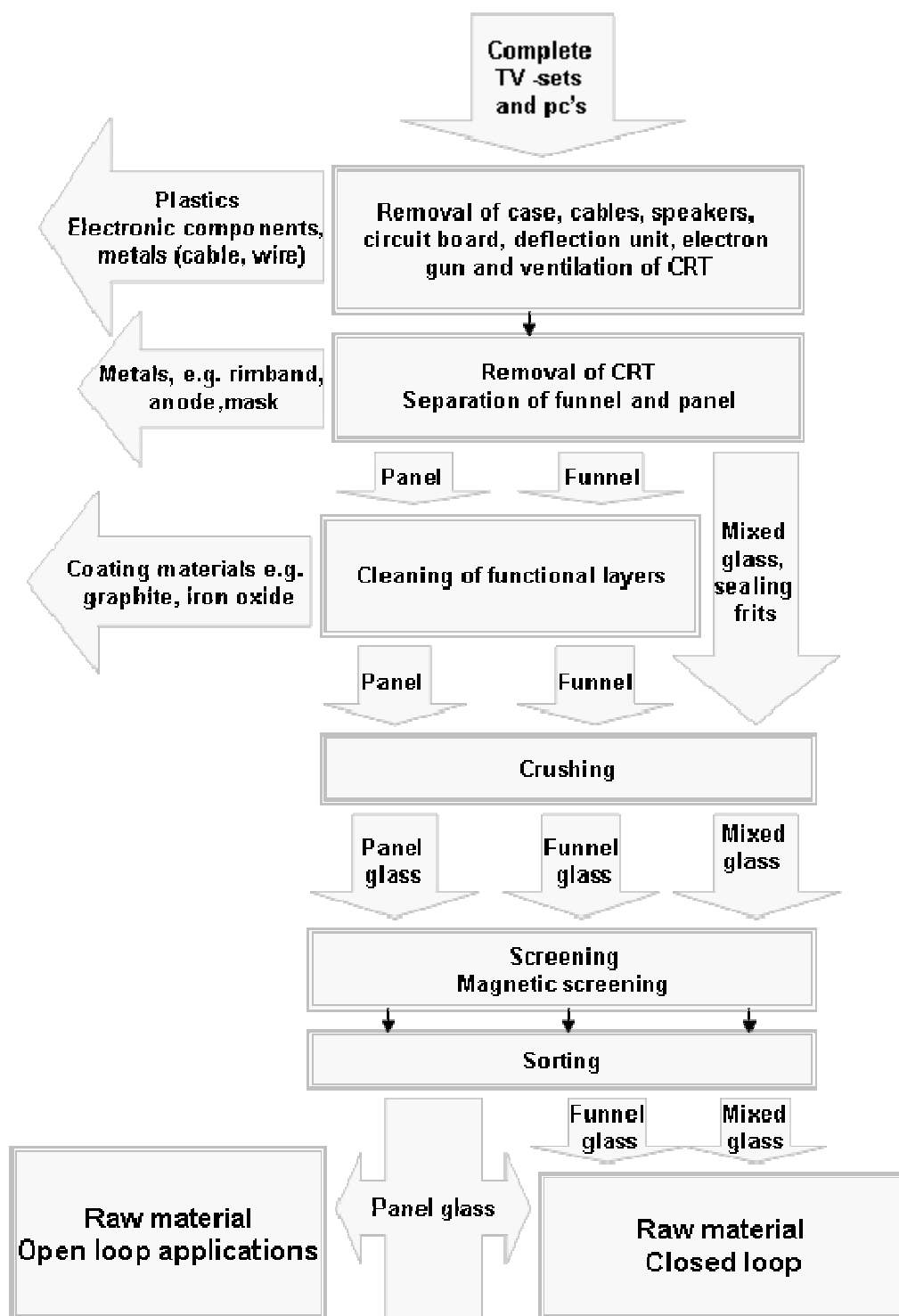


Figure 2. Process flow to generate raw material from End-of-Life TV and PC devices containing Cathode Ray Tubes (adapted from Döring 2002)



With re-use of materials from EEE, we are still in many ways in the very beginning. Closed-loop recycling can utilise only a part of the materials entering from recycling programs. Only a few applications for open-loop recycling have been studied or established for industrial scale re-use of materials coming from EEE.

### **1.3. Environmental Concerns Related to CRTs**

Loss of materials, concerns about harmful substances in materials being landfilled and occupational health issues in recycling operations have been main environmental concerns related to WEEE. The harmful substances present in devices containing a CRT are an important issue when equipment is landfilled or incinerated. Many of the substances that cause environmental concerns in recycling and disposal of screens are used for the purpose of minimising risks to human health during product use. Substances of environmental concern in devices containing a CRT include antimony, barium, beryllium, cadmium, chlorine, and/or bromide, lead, lithium, mercury and phosphorus. Harmful substances found in glass parts of CRTs are lead, barium and phosphorus. Older models of CRTs can also contain fluorine and arsenic, which were used as refining agents. Additionally, antimony has been used for this purpose up to present production. (OECD 2002, Guy-Schmidt and Thamin 1998)

In the glass parts of CRTs, the funnel part is made out of glass containing 11–24 weight-% of lead. Lead is used in the funnel to protect the users of devices from harmful x-rays. There is no technical substitute for lead in CRT glass. Lead is encapsulated in glass and will not be released until the glass is broken into small pieces and exposed to aqueous solutions, where dissolution of lead ions will take place. In landfilling, the conditions of lead dissolution exist. (OECD 2002, CREED 1997)

Fluorescent coatings, like phosphors (typically zinc sulphide and rare earth metals), are used on the inner surface of a CRT screen to convert the kinetic energy of the electron beam to light. Barium oxide is used in the getter plate of the electron gun of CRTs and is encapsulated in glass materials. Some old CRT glasses may also contain some antimony. The recycling of CRTs, when material separation and removal of coatings is performed with high-quality process, prevent these

harmful materials from entering landfills or environment. Instead of producing waste materials, recycling can be used to provide a wide selection of high-quality secondary raw materials to various industrial applications. (OECD 2002, Guy-Schmidt and Thamin 1998)

In the dismantling process of products, knowledge of harmful substances is crucial for the occupational health in companies operating the recycling procedures (Manninen 2002).

#### **1.4. Legislative Responses Steering Recycling of CRTs**

Europe has been in many terms a forerunner in research and development of WEEE recycling as well as in emphasising the recycling with legislative responses. Key legislative initiatives that favour the reuse and recycling of cathode ray tube glass materials are a Directive of the European Parliament and of the Council on Waste Electrical and Electronic Equipment (WEEE) and the Decision of the Commission of the European Communities on the list of wastes. Also the Directive of the European Parliament and of the Council on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (ROHS) promotes recycling of materials from WEEE. (European Union 2003, Häkkinen 2002)

Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on Waste Electrical and Electronic Equipment (Official Journal L 37 of Feb 13, 2003) was amended by Directive 2003/108/EC (Official Journal L 345 of Dec. 31, 2003). According to this directive (the European directive on Waste from Electrical and Electronic Equipment), Cathode Ray Tubes have to be removed from separately collected WEEE for selective treatment. The fluorescent coating has to be removed from the Cathode Ray Tubes. For WEEE falling under categories IT & Telecommunication Equipment and Consumer Equipment, the rate of recovery shall be increased to a minimum of 75% by an average weight per appliance. Component, material and substance re-use and recycling shall be increased to a minimum of 65% by an average weight per appliance. In practise, this means that Cathode Ray Tube glass must be recycled in order to reach the recycling target for discarded televisions and monitors.

Member States of the European Union are responsible for “minimising the disposal of waste electrical and electronic equipment (WEEE) as unsorted municipal waste and are to set up separate collection systems for WEEE. In the case of electrical and electronic waste, Member States are to ensure that, as of 13 August 2005:

- final holders and distributors can return such waste free of charge
- distributors of new products ensure that waste of the same type of equipment can be returned to them free of charge on a one-to-one basis
- producers are allowed to set up and operate individual or collective take-back systems
- the return of contaminated waste presenting a risk to the health and safety of personnel may be refused

Producers must make provision for the collection of waste which is not from private households. Member States must ensure that all waste electrical and electronic equipment is transported to authorised treatment facilities.” According to the WEEE directive, the symbol indicating separate collection for Electrical and Electronic Equipment (see Figure 3.) must be printed visibly and legibly on all EEE products.



Figure 3. The symbol indicating separate collection

By December 31, 2006 at the latest, a rate of separate collection of at least 4 kg on average per inhabitant per year of Waste Electrical and Electronic Equipment from private households must be achieved. A new target rate to be achieved by December 31, 2008 is to be specified later.

The Decision of the Commission of the European Communities on January 16, 2001 amending decision 200/532/EC as regards the list of wastes was published on February 16, 2001 (Official Journal). According to the amended list of wastes, discarded electrical and electronic equipment containing hazardous components such as glass from Cathode Ray Tubes are classified as hazardous waste. This is going to influence transportation, storage and disposal method of end-of-life CRTs (Häkkinen 2002).

Recycling of materials from WEEE is promoted also by the Directive of the European Parliament and of the Council on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (ROHS), Directive 2002/95/EL of 27 January 2003 (Official Journal L 37/19 of Feb 13, 2003). Substances that entail human health and environmental concerns are materials like brominated flame retardants (BFR), cadmium, lead and phosphors. (European Union 2003)

The European Commission has adopted a Communication on Integrated Product Policy (IPP), outlining its strategy for reducing the environmental impact caused by products. Integrated Product Policy (IPP) seeks to minimise environmental degradation from manufacturing to disposal of the products by examining all the phases of a product's life-cycle. IPP aims at stimulating each actor of the production process, such as designers, industry, marketing people, retailers and consumers. (European Commission 2003, Charter et al 2001)

## **1.5. Glass Recycling as an Academic Theme**

As a research area, recycling issues are young academic subjects, even though material recycling has been identified to be one of the key issues in sustainable development.

Research on the applications and possibilities for material re-use is done mainly by materials at institutions of material technology. What comes to glass, material technology research belongs to inorganic chemistry. In addition to research initiatives in this field that are being carried out at universities, a growing number of companies specialising in environmental technology have played an important role in the development of this field.

Academic writing under the theme of recycling relates to wide range of issues within many fields of research, because of the broadness of the theme. From the viewpoint of material, two compiled publications have summarised the academic research carried out in glass recycling: *Recycling and Reuse of Glass Cullet* (edited by Ravinda k. Dhir, Mukesh C. Limbachiya, Thomas D. Dyer, Thomas Telford Publishing, London, 2001) and *Glass Waste* (ed. Mukesh C. Limbachiya and John J. Roberts, Thomas Telford Publishing, London, 2004). Separate articles about glass material re-use and possible applications have been published in literature related to re-use of various waste materials and in journals of glass/ceramic material and journals of production technologies of glass and ceramics.

## 2. Existing Recycling Routes for Glass Materials

As a material, glass is ideal for recycling – it is theoretically 100 % recyclable. In most cases, glass can be used repeatedly without any notable changes in its physical properties. In recent years, new legislation has also contributed to an increase in glass recycling.

Recycling of a waste material can aim at the utilisation of a material to the same production from where it originated. This is referred to as closed-loop recycling. Alternatively, waste material can be utilised to new products. In this case, the recycling route is open-loop recycling. Closed-loop recycling is a common practice in glass industry, having many environmental and economical advantages. The existing open-loop recycling of glass waste is mostly based on the utilisation of container glass. To some extent, other glass products, like flat glass and special glasses, are also used to manufacture products out of recycled glass.

### 2.1. Recycled Glass as a Raw Material in Glass Industry

Glass recycling has been common practice in glass manufacture throughout the history of glass making: rejected production, so called cullet, has been re-melted to be used as a part of the batch (see Figure 1 for process waste). This practice has many advantages besides reducing the amount of waste: it saves virgin raw materials and melting energy, gives better melting properties to the batch and reduces furnace emissions (Tooley 1984).

Advantages of using cullet in glass melting can be seen in all glass melting processes, regardless of type of the glass production or furnace used for it. Recycling of container glass has been the most visible development in glass recycling for consumers. Glass recycling has grown rapidly since the early 1970's when the bottle bank systems were introduced into several European countries. (Reynolds 2002).

A growth of 4.6% in year 2003 was achieved in collection of container glass

in the European countries with the total amount of 9.376 000 tons. Another important source of waste glass generated is Waste of Electronic and Electrical Equipment, since glass makes up about 70–80% by weight of devices containing Cathode Ray Tubes. Additionally, a growing amount of other recycled glass products, like windscreens and window glass, comes to the recycling markets. Especially the new requirements on automotive parts recycling, with the goal of 80% by weight, generate a need for open-loop windscreen recycling.

Recycling rates have improved significantly, achieving a new high average of 60% in year 2003 in the European countries. (FEVE 2004). Recycled glass materials are mainly used as a secondary raw material for closed-loop applications. However, these applications can not utilise all of the recycled glass. Consequently, there is a need for new open-loop applications for collected glass materials.

Recycled glass material is used in two different ways in glass industry, where a distinction between factory and foreign cullet is made. Factory cullet is the waste glass material from the plant's own production, which is returned to the melting process. Foreign cullet is end-of-life glass, which has been collected from various sources and contains material from many manufacturers. Factory cullet is regarded as a "safe" raw material: the material is treated and directly returned to the melting process, which eliminates any risks of contamination. Factory cullet can also be regarded as an economical raw material, because it causes no transportation or storage costs, which are significant expenses when using foreign cullet. Heat of reaction needed for the batch reactions is already consumed in the first melting, which enables saving of energy in melting. (Reynolds 2002, Tooley 1984, Keller 1984, Cable 1984).

The current applications for recycled cullet are mainly applications utilising container glass. The collection system for glass containers is an established practice in many countries. For instance in Finland, these operations cover the whole country. Glass material is collected divided into clear and coloured fractions. Further, automatic cleaning and crushing systems are used. Container glass has a fairly stable chemical composition, mainly because of the fast, automatic production method that is best suited for a narrow compositional range. All of these factors are favourable for industrial-scale utilisation of this material.

In glass production, the use of foreign cullet always brings along the risk of contaminations. Glass material from collection always contains some impurities that can have an undesired effect on glass melting or change the quality of the products. Table 1. indicates the maximum allowed impurity levels usually applied to recycled container glass. Harmful effects on the glass melting and quality of glass products caused by contaminations are mainly failures in the optical properties, mechanical strength or colour of the glass. The effects of different impurities on appearance and properties of glass are listed in Table 2. (Dhir and Dyer 2004, Reynolds 2002)

The varying chemical composition of the recycled glass, consisting of products from different manufacturers, can also bring along some changes in the composition of the products where it is utilised. The compositional differences have to be balanced by changes in the batch in order to achieve the desired composition in the product. For this reason, foreign cullet requires a careful optimisation of the total batch composition to guarantee a controlled melting process and a product with desired properties. According to the type of glass production, the theoretical maximum for cullet addition to the melt varies. (Cable 1984)

Cullet treatment technology has been improved significantly with the growth of glass recycling. The sorting efficiency and cullet quality have been enhanced, which means that the costs for cullet treatment have been minimised. (Frisch 1996)

Table 1. Maximum impurity levels of collected container glass  
(Dhir and Dyer 2004, Reynold 2002)

Ceramic, mineral, porcelain (CMP)	< 25 g/t
Aluminium	< 5 g/t
Ferrous metal	< 5 g/t
Lead	< 1 g/t
Organics	< 500 g/t
Moisture	< 2 %



Table 2. Cullet contamination and impurities and their influence on glass appearance and properties. (Dhir and Dyer 2004, Reynold 2002)

<b>Impurity</b>	<b>Effect on glass</b>	<b>Effect on quality</b>
<b>Other glass type</b>	Unmelted particles	Weakened product
<b>Other glass colours</b>	Colour streaks Seeds, blisters	Colour failures Optical failures
<b>Ceramics</b>	Unmelted particles, stones	Weakened product Optical failures Redox issues
<b>Magnetic metals</b>	Seeds, blisters	Weakens glass Optical failures
<b>Non magnetic metals</b>	Unmelted parts Seeds, blisters	Weakens glass Optical failures
<b>Organic components</b>	Colour failures Seeds, blisters	Colour failures Optical failures
<b>Moisture</b>	Seeds, blisters	Handling problems Unightly

## 2.2. Cullet as a Raw Material in Ceramic Industry

Ceramic industry, especially production of construction materials, uses large quantities of non-renewable raw material to produce a large variety of fired structural products. Manufacture of ceramics has been widely studied as an environmentally sound possibility to utilise both waste materials and industrial by-products. Various waste materials have been introduced as a raw material for different ceramic structural products. These include ashes from various industrial or municipal combustion processes, paper sludge (both from recycled product and virgin cellulose sources), water and waste-water treatment sludges, container glass waste and sludges from ceramic processes (Moedinger and Andersson 2001, Niemelä 1999, Sevelius 1997).

Ceramic tiles are one example of products where waste container glass cullet has been used in an industrial-scale production. The amount of glass addition varies depending on the other raw materials and firing method used. As large amounts as 70 wt-% of waste glass have been successfully introduced to a new type of ceramic tile commercially available. In forming of this tile a high pressure is applied. Tiles are fired at 1000°C, which is about 200°C lower than the firing temperature of the corresponding ceramic product without the glass addition.

Beside the energy and virgin raw material savings brought by the use of waste glass, carbon dioxide emissions from manufacturing are estimated to be reduced by 26% (Kyoko 2001).

The raw material requirements for materials in ceramic industry vary widely according to the production process and products. Some product groups, such as bricks made of earthenware, tolerate a wide range of secondary raw materials, unlike whiteware, which has very strict purity requirements. Raw material purity is important in production of whiteware. Most of the possible contaminations that recycled glass material can bring along have a colouring effect to the ceramic whiteware. (Ryan and Ratford, 1997).

### **2.3. Existing Open-Loop Applications for Recycled Glass**

Current open-loop applications for glass waste are mainly applications utilising container glass. Beside the closed-loop use as a raw material for new packages, recycling routes using glass as a raw material in production of insulation material and sheet glass have been introduced. These applications can utilise considerable amounts of recycled material. For instance, in production of glass wool, up to 80 wt-% addition of recycled material can be added to the batch. (the Environmental Register of Packaging PYR Ltd 2004, Suomen keräyslasiyhdistys 2004).

In other fields of construction, recycled glass material has been used as aggregate in concrete. Numerous studies have dealt with the problematic alkaline-silica reaction (ASR) in glass-concrete mixtures (Dyer and Dhir. 2001, Zhu and Byars 2004). ASR is the reaction between the alkali in the concrete and the silica in the glass. This reaction causes expansion of concrete, which may lead to cracks. This reaction has been successfully controlled in studies e.g. by adjusting the particle size of glass material or chemically by lowering the alkali content of concrete (Shao 2001, Meland 2001).

For construction purposes glass waste has been used for lightweight fill material by foaming process (Brusatin et al 2004, Aabøe and Øiseth 2004). Other possible applications for foamed glass are use as insulation or ground improvement material (Dhir and Dryer 2004). Foaming of recycled glass materials is usually performed

by adding particles of foaming agents, such as silicon carbide which release gas at elevated temperatures (Onitsuku et al 2001).

Construction blocks and tiles have been manufactured from recycled container glass. The production can be based on glass melting and forming the products by e.g. casting. Sintering is another process requiring less energy than glass melting. Sintered glass products have been manufactured with some additives or ceramic raw materials. Also tiles containing recycled glass have been formed by using resins as a binder for glass particles. (Beylerian and Dent 2005, Recycling Business Assistance Center 1996, Rematerialise 2002, Eco-Wise 2005, Lipford 2005)

Alternative uses for recycled packaging glass where the glass material has been used as a cullet crushed to the particle size needed, include applications as filtration medium and abrasive material. In filtration, fine solids are usually removed from waste water using filtration materials like quartz and anthracite. Glass is a chemically inert and not micro-porous material. Consequently, it has been found to be an excellent material for water filtration. Applications include the filtration of drinking water, sewage treatment, aquariums, swimming pools and industrial water.

Recycled glass has also been reported as a potential material to replace the use of silica sand, metal slags or aluminium oxide as an abrasive material. Glass has been found suitable for both wet and dry processes when using size fractions finer than 1.68 mm (Pascoe et al 2001). Crushed glass material can be superior to traditional abrasives as for its cutting efficiency and working safety. Glass contains virtually no heavy metals causing health risks or crystalline silica causing silicosis. Grain sizes used in abrasives vary from fine grits of 0.00–0.75 mm to coarse grits of 1.00–3.00 mm.

Recycled glass has also been used as decorative aggregates. Aggregates are produced by melting and in many cases also by colouring the recycled glass. Glass is cast and after cooling it is crushed to aggregates with sizes varying from 1 to 18 mm. Aggregates are used in construction and landscape architecture for e.g. pavings, gardens and graveyards.

Moreover, an alternative use for glass waste has been found as filler in asphalt. In this so called glasphalt, the amount of recycled glass is typically 10–15 wt-%.

Recycled glass has also been tested as an additive in paints for road signs. Glass addition is reported to enhance the light reflections, giving higher illumination for the road instructions. (Chang et al 2001, Fitzsimons and Gibney 2004).

Recycled glass can also be used as a source of minerals or sodium silicate. Extraction of silica and sodium silicate from recycled glass has been studied by Di Bella et al (2003) and Corigliano and Mavilia (2001).

In small and medium-sized enterprises, packaging glass is also reused by reforming packages to new products by cutting and polishing or by melting the glass material, often with some additives to enhance the glass refining, and forming it again to a new product. Products like wine glasses, jars, pitchers and lampshades have been made out of used wine bottles (see Photo 1) (Lefteri 2002, Fuad-Luke 2002). Recycled glass materials are also used to form jewellery products. Recycled glass has also inspired artists who have used it as a raw material (Kirk 2001) or as ready-made glass objects that make up a part of or an entire work of art.



Photo 1.  
Recycled container glass used  
as a material for new products.  
Designer Jukka Isotalo.  
Photo by Tanja Ahola.

### 3. End of Life Cathode Ray Tubes

The stringent quality requirements for very precise colour control in displays place strict demands on CRT glass. Thus, CRT glass is of high quality and manufactured from well-purified raw materials. The amount of glass material in CRTs has changed with technological development. In TV sets, the amount of glass material has recently been increased because of larger screen sizes that have been introduced in the new models. Additionally, flat screen technology requires a thicker glass than the curved screen in order to counteract the strength reduction due to the loss of the inherent strength.

#### 3.1. Glass from Cathode Ray Tubes

The CRT glass types are special glasses, the properties of which are reached through the specified chemical composition. Beside the basic glass materials, the raw materials include also expensive components, e.g. rare earths that render special characteristics to the glass. The chemical composition of the glass material varies according to the producer, age of the CRT and the source (PC or TV, whether a black and white or colour device). The compositions have changed as cathode ray tube technology has been developed. Further, each monitor is made out of two main glass parts of different chemical composition: the front part, i.e. the panel made of lead-free glass and the funnel containing lead (see Photo 3). In general, the panel glass is lead-free, with the exception of production originating in the United States: addition up to 3 wt-% of lead oxide is used there for panel glass. Panel and funnel parts are sealed together with a glass solder fit containing up to 85 wt-% lead oxide. The parts of CRT and their special characteristics that are important for recycling are summarised in Table 3.

Table 3. Parts of CRT with their special characteristics and glass type

Part of CRT	Glass type	Special characteristics
Panel	Lead-free	Front, visible part of CRT
Funnel	Leaded	The backside of CRT
Neck	Leaded	Contains electronic gun
Stud	Leaded	Contains electrical contacts
Glass solder	Leaded	Frit sealing the panel and the funnel parts

The main parts are the panel, i.e. the visible part of cathode ray tube, which makes up about 2/3 of the total mass of the CRT, and the funnel, which corresponds to 1/3. With the exception of the panel, the content of lead oxide of these glass types varies from 10 to 85 wt-%. The lead content in funnel is 11–24 PbO wt-%, and the sealing frit connecting the two main parts contains up to 85 w-% PbO. Black and white monitors contain one glass composition only, consisting 3 wt-% of lead oxide. Thus, only the lead-free panel from colour devices is a possible raw material for open-loop applications.

The CRT also contains many non-glassy parts: the metallic shielding, the shadow mask and the electron gun. The mask is assembled with metallic pins which are molten into the glass and the acceleration voltage is applied through a metallic button molten into the funnel glass.

Both the panel and the funnel are coated with layers containing several components, e.g. metal oxides, rare earth oxides and graphite. These components must also be removed before recycling can take place. These functional layers are:

- fluorescent layer on the panel glass, consists of zinc sulphides and rare earth oxides
- aluminium plating on the backside of the fluorescent layer
- graphite layer on the outside of the funnel
- iron oxide layer on the inside of the funnel

In old CRTs, also some cadmium can be found in the fluorescent layer.



Photo 2. Production of panel parts. Photo: Schott AG.



Photo 3.  
Funnel and panel parts of  
Cathode Ray Tube.  
Photo: Schott AG.

### 3.2. Properties of CRT Glass Materials

The CRT glasses are special glasses characterised by the oxide composition levels and physical properties shown in Tables 4. and 5. The chemical composition has been adjusted through many changes along the developments in CRT technology. Additionally, technical demands in the production of CRTs have affected the glass composition. Table 4 shows the minimum and maximum levels as well as the difference of different oxides of funnel and panel glass compositions between years 1997–2001.

Table 4. Range of chemical composition of panel and funnel glass.  
Compositions are from lots collected for closed-loop use and analysed by CRT manufacturer (method of analysis: XRF).

%	Panel glass			Funnel glass		
Oxide	Min	Max	Difference	Min	Max	Difference
SiO <sub>2</sub>	58.85	65.40	6.55	51.19	63.45	12.26
Al <sub>2</sub> O <sub>3</sub>	1.20	3.70	2.50	1.10	5.00	3.90
Na <sub>2</sub> O	6.15	9.80	3.65	5.25	8.05	2.80
K <sub>2</sub> O	6.00	8.95	2.95	7.15	10.30	3.15
Li <sub>2</sub> O	0.00	0.50	0.50	-	-	-
F	0.00	0.83	0.83	-	-	-
BaO	1.90	14.20	12.30	0.00	3.00	3.00
SrO	0.00	11.60	11.60	0.15	0.65	0.50
CaO	0.00	4.55	4.55	1.60	4.45	2.85
MgO	0.00	1.95	1.95	0.90	3.00	2.10
As <sub>2</sub> O <sub>3</sub>	0.00	0.30	0.30	0.00	0.15	0.15
Sb <sub>2</sub> O <sub>3</sub>	0.18	0.70	0.52	0.02	0.35	0.33
TiO <sub>2</sub>	0.00	0.60	0.60	-	-	-
CeO <sub>2</sub>	0.00	0.55	0.55	-	-	-
PbO	0.00	3.25	3.25	11.60	24.60	13.00
ZrO <sub>2</sub>	0.00	3.50	3.50	0.20	0.20	0.00
ZnO	0.00	0.65	0.65	-	-	-
Fe <sub>2</sub> O <sub>3</sub>	0.03	0.07	0.04	fig. in weight-%		

Table 5. Calculated values for physical properties of panel and funnel glasses

Property	Panel glass	Funnel glass
Linear expansion coefficient	$10 \times 10^{-6} \text{ 1/K}$	$9,8 \times 10^{-6} \text{ 1/K}$
Density	2.78 g/cm <sup>3</sup>	3.0 g/cm <sup>3</sup>
Working point	approx. 1000 °C	ca. 960 °C
Transformation temperature	approx. 500 °C	ca. 460 °C
X-Ray absorption	From 17>28 cm-1	From 33 >65 cm-1



### 3.3. Open-loop Recycling of EOL CRTs

The application areas should be chosen to benefit from the high quality of CRT glass in order to facilitate a cost-effective open-loop recycling. The costs for dismantling and cleaning processes can decrease the competitiveness of CRT glass as a secondary raw material in applications where large amounts of conventional minerals are used.

Table 6. Analysed chemical compositions of EOL CRT colour panel glasses, a typical tableware glass and container glass. The chemical compositions of EOL CRT glasses are materials used in test series (collected in Finland during 2001–2002). Viscosity values are based on the model by Lakatos (1976) and the other properties on the models by Appen (1960).

Oxide	CRT panel glasses			Commercial tableware glass <sup>1</sup>	Container Glass <sup>2</sup>
	Colour PC	Colour TV	Mix	wt-%	wt-%
SiO <sub>2</sub>	60.3	61.6	61.4	69.0	72.3
Al <sub>2</sub> O <sub>3</sub>	2.37	3.26	3.17	0.37	1.57
Na <sub>2</sub> O	8.36	8.57	8.45	10.2	13.48
K <sub>2</sub> O	7.55	7.36	7.11	7.4	0.8
Li <sub>2</sub> O	-	-	-	0.19	-
MgO	0.19	1.05	0.99	0.035	0.79
CaO	0.96	2.30	2.14	3.6	10.73
ZnO	0.23	0.08	0.12	2.26	-
BaO	8.87	10.52	10.51	5.3	-
B <sub>2</sub> O <sub>3</sub>	-	-	-	1.23	-
Fe <sub>2</sub> O <sub>3</sub>	0.22	0.058	0.058	0.029	0.047
SrO	9.25	3.81	4.28	-	-
Sb <sub>2</sub> O <sub>5</sub>	0.44	0.57	0.62	-	-
As <sub>2</sub> O <sub>5</sub>	0.03	0.11	0.08	-	-
PbO	0.011	0.32	0.060	-	-
<b>T/°C</b>	<b>log (η/dPas)</b>				
500	12.89	13.40	13.44	13.24	18.80
600	9.59	9.81	9.85	9.53	12.51
700	7.51	7.60	7.64	7.31	9.23
800	6.09	6.10	6.14	5.83	7.21
900	5.05	5.02	5.05	4.77	5.85
1000	4.25	4.20	4.23	3.98	4.86
1100	3.36	3.56	3.59	3.36	4.12
1200	3.13	3.05	3.07	2.87	3.54
1300	2.71	2.62	2.65	2.47	3.07
1400	2.36	2.27	2.29	2.13	2.69
1500	2.07	1.97	1.99	1.85	2.37
<b>Exp (1/K)</b>	10.07-06	10.20-06	10.07-06	99.70-07	8.5-06
<b>Density (g/cm<sup>3</sup>)</b>	2.5733	2.6269	2.6191	2.555	2.5
<b>Refr. index</b>	1.5155		1.5233	1.5222	1.520

<sup>1</sup> Source: Tableware glass producer

<sup>2</sup> Source: Smrček 2005: Average composition of container glass in Finland 1981-1990

In open-loop applications, the CRT glass cullet must be lead-free, and should thus be based on the use of colour panel glass. The oxide compositions of panel glasses for colour PC and colour TV are compared with tableware (Paper III) and container glass (Paper IV) compositions. Calculated values for several physical properties of the glasses given in Table 6. indicate that the glasses have similarities in viscosity temperature behaviour. Similarities were found also in their other properties.

In ceramic industry the CRT glasses, however, could be applicable in many processes as secondary raw materials. The comparison of ceramic raw materials to the composition of CRT glass materials gives one possibility to introduce secondary raw material to the manufacturing process. When comparing the composition of typical Finnish feldspars with panel glasses, the oxides are at the same level also in respect to the colouring agent  $\text{Fe}_2\text{O}_3$ , c.f. Table 7. Thus, CRT panel glass could be an alternative to feldspars in ceramic production, including whiteware, in case the addition of CRT glasses are at a level which does not adversely affect the desired properties of products (Paper II).

Table 7. Typical compositional range (wt-%) of panel glasses as well as two Finnish feldspars (SP Minerals Oy Ab 1998) used for ceramics production.

Oxide	Panel glass min-max* wt-%	Finnish FFF Feldspar wt-%	Finnish Alavus Feldspar wt-%
$\text{SiO}_2$	58.85-65.40	67,2	72,0
$\text{Al}_2\text{O}_3$	1.20-3.70	18,3	15,7
$\text{Fe}_2\text{O}_3$	0,03-0.07	0,13	0,03
$\text{TiO}_2$	0,00-0.60	-	-
$\text{CaO}$	0.00-4.55	0,5	0,2
$\text{MgO}$	0.00-1.95	>0,03	>0,03
$\text{Na}_2\text{O}$	6.15-9.80	5,0	3,7
$\text{K}_2\text{O}$	6.00-8.95	7,7	7,5

\* + BaO 1.90-14.20, PbO 0.00-3.25,  $\text{Sb}_2\text{O}_3$  0.18-0.70, ZnO 0.00-0.65,  $\text{ZrO}_2$  0.00-3.50,  $\text{As}_2\text{O}_3$  0.00-0.30,  $\text{TiO}_2$  0.00-0.60,  $\text{CeO}_2$  0.00-0.55

### 3.4. EOL CRT Glass Processing for Recycling

Recycling of the CRT glasses requires a careful separation process, in which the black and white monitors and the funnel and neck parts of the colour monitors are sorted out from the lead-free panel glass. Coatings are separated from the inside surfaces of funnel and panel.

In the RECYTUBE-project, different dismantling and cleaning techniques were studied. For dismantling of the glass parts of CRT, diamond cutting was tested. Dismantling can also be done by hot-wire technique, where a heated wire is tied around the CRT. The thermal shock separates the panel and funnel parts. (Scmid 1999)



Photo 4.  
Dismantling of the funnel and panel parts by hot-wire technique.  
Photo: Ekokem Oy Ab



Photo 5. Dismantling of funnel and panel parts by laser cutting technique in the Proventia Automation Oy's plant.  
Photo: Proventia Automation Oy

In this project, also technical and economical viability of optical sorting of glass was tested. The development of optical sorting resulted to a sorting machine capable to produce 9 tons/hour of a glass containing less than 1 wt-% of foreign glass with undesired composition.

Later new techniques have been developed for the dismantling of CRT glass, such as laser dismantling which has been developed in Finland to an industrial-scale production line(see Photo 5.)

### **3.5. Raw Material Requirements for Open-Loop Applications**

For the utilisation of recycled CRT glasses in ceramic and glass industry, the most important raw material requirements are the following:

- chemical composition of the glass
- compositional limits for the glass
- purity of the glass
- particle size
- particle form
- humidity
- size of the lot

Chemical composition of the glass determines the properties, both during manufacture and the properties of the finished product. Table 8. shows average CRT panel and funnel composition in comparison with commercial tableware glass and container glass. Papers I–V further describe the compositional requirements for specific applications.

The most important characteristic related to glass manufacture is the temperature-viscosity dependence. The lower the temperature at which the viscosity is studied, the more significance the composition of glass has. The most important viscosity values related to different glass forming operations (Cable 1991) are summarised in Figure 4.

At high temperatures, around 1400°C, the viscosity of commercial glasses is 100–1000 dPas. Melting is usually performed at this viscosity favouring the

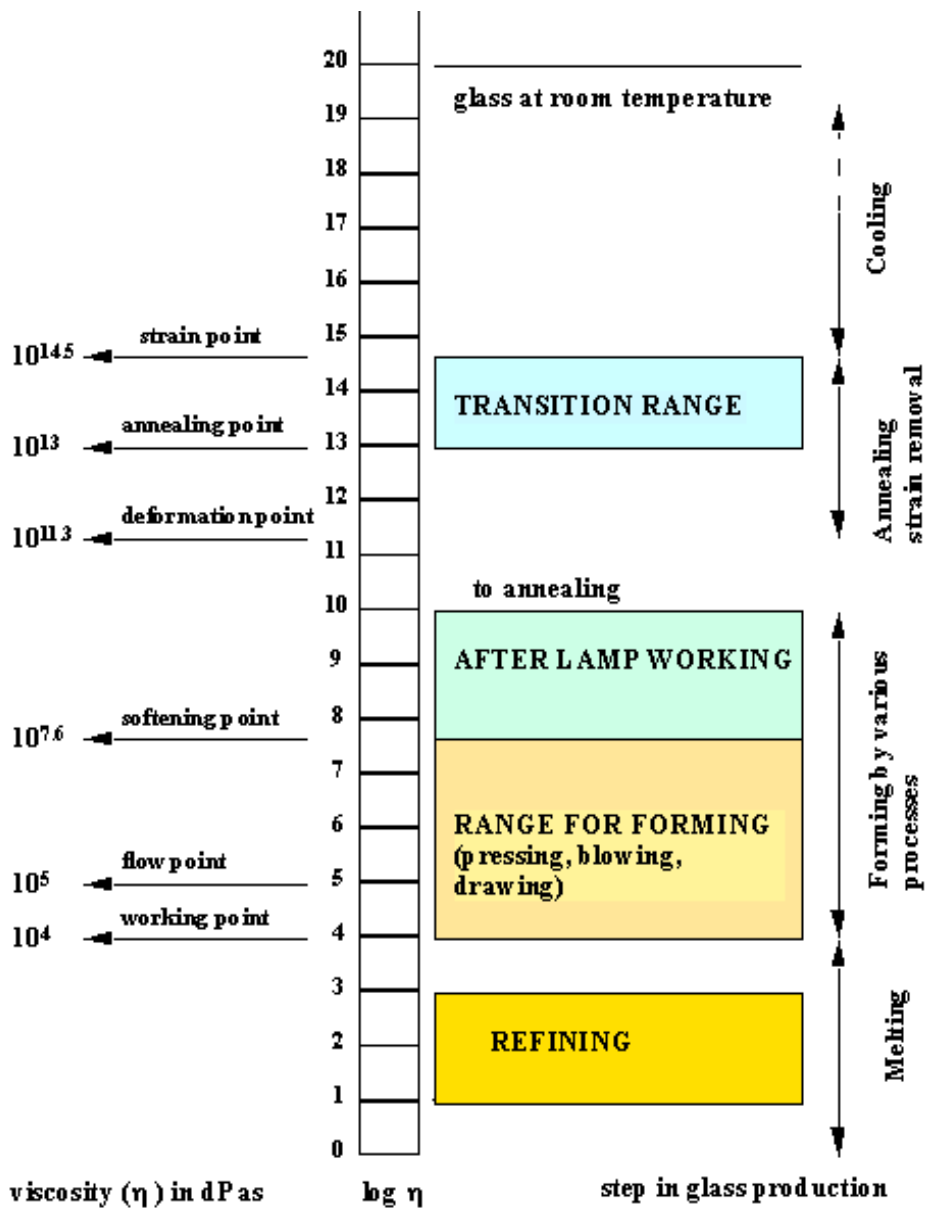


Figure 4. The viscosity ranges (Cable 1991) of different glass operations

physical refining, i.e. disappearance of the gas bubbles by merging and rising to the melt surface. If the melting temperature is higher than that corresponding to viscosity of 100 dPas, corrosion of refractory material is increased by the low viscosity of melt.

At the beginning of the working range the temperature is about 1200–1100°C. The "upper end" of the working range refers to the temperature at which the glass is ready for working (generally corresponding to a viscosity of 1000–10 000 dPas), while the "lower end" refers to the temperature at which it is sufficiently viscous to hold its formed shape (generally corresponding to a viscosity exceeding 10 000 dPas). Usually the working range of glass is referred to as the viscosity range from 1000–1000 000 dPas.

While the temperature decreases, the viscosity of the melt increases at a fairly constant rate at the beginning. At temperatures below 1000°C the viscosity increases strongly. The glass must be shaped before it starts to crystallise which starts at the liquidus temperature of glass. The softening point temperature corresponds to a viscosity of 10 <sup>7.6</sup> dPas.

Table 8. Calculated temperature-viscosity values for a typical tableware, container and an average CRT panel glasses based on the models by Lakatos et al (1976).

T/°C	log( $\eta$ /dPas)		
	Typical tableware glass	Container glass	CRT panels, average
500	13.22	18.80	13.15
600	9.24	12.51	9.50
700	6.96	9.23	7.29
800	5.48	7.21	5.81
900	4.44	5.85	4.78
1000	3.67	4.86	3.94
1100	3.07	4.12	3.32
1200	2.60	3.54	2.81
1300	2.22	3.07	2.40
1400	1.90	2.69	2.06
1500	1.64	2.37	1.77

After completed working, glass has to be cooled to a temperature around 500–600°C fairly quickly in order to avoid crystallisation. From this temperature the cooling is performed according to a certain temperature–time curve to room temperature. During annealing process the structural tensions that build up while shaping and cooling are removed from the product.

In literature, several models describing the compositional dependence of viscosity as function of temperature can be found, such as models by Lakatos et al (1976). According to this model, calculated temperature–viscosity values for compositions of typical tableware, container and average CRT panel glasses are shown in Table 8.

Commercial soda lime glasses expand when heated and contract when cooled. This thermal expansion varies according to the chemical composition of glass. It is necessary to know the coefficient of expansion when two glasses with different chemical compositions are to be joined to a single piece of ware or when glass is joined to another material.

Other properties of glass material important to glass manufacturing are elastic properties, heat capacity and thermal conductivity. In the final use of the product, the most important properties are usually mechanical, chemical and thermal durability along with optical properties.

Table 9. Thermal expansion values, calculated according to the model by Appen (1960), for typical tableware, container and CRT panel glass.

	<b>Commercial tableware glass</b>	<b>Container glass</b>	<b>CRT panels, average</b>
Thermal expansion exp (1/K)	99.7 x 10 <sup>-7</sup>	85 x 10 <sup>-7</sup>	99 x 10 <sup>-7</sup>

## 4. Experiments

### 4.1. Methods

This study has been carried out under experimentalist research position. The plan for the preliminary experiments was based on a literature survey. The background information on raw material requirements in different ceramic and glass productions has been collected from literature and from European ceramic and glass industry. Literature study covered the application areas for re-use of the waste glass material and patents related to the recycling of CRT glasses.

According to the literature, the applications in which recycled glass materials was used in an industrial-scale productions, were based mainly on the utilisation of container glass. Patents (up to January 2003) related to the subject, were mainly on new technical solutions for dismantling and cleaning processes. In terms of application areas, very few of them were connected to CRT utilisation in open-loop recycling. Process ideas of converting CRT glass to forms of glass granulates were identified, too (patents DE19702560 A 19980730 and DE4332532 A 19950112).

Focusing on the special features of CRT glasses, the final experimental scheme was drawn up and the applications tested were chosen by on the basis of preliminary tests and literature survey. Know-how from work experience in manufacturing of ceramic and glass products and research tradition in the Department of Ceramics and Glass at UIAH were also significant factors for examining possible applications for CRT glass utilisation.

On laboratory scale, the following application areas related to ceramic industry were tested:

- use as raw material for high-fired glaze:  
substitution of feldspar
- use in low-fired glaze: substitution of frits
- use as a raw material in clay body:  
substitution depending on the type of clay



Concerning glass industry, the following areas were tested on laboratory scale:

- tableware glass: use as a raw material for tableware products
- use as a base material for coloured glass production
- the production of glass tiles
- base material for glass tiles
- coating material for the construction blocks made out of container glass

In the laboratory-scale testing, the use of CRT glass as a raw material for clay-body was found to be a possible area for CRT use. However, it was found to be affected highly by the type of clay-body and manufacturing process. Thus, the variables for test series were too many for further study. The CRT use as a base material for coloured glass was found to be another possible area of utilisation with most colouring agents, enhancing their colouring power. However, there were exceptions to this, such as colouring the glass with manganese oxide, MnO. The colouring effect of manganese oxide was fading, when CRT glass was used as a base material. The background work and test results from these series are summarized in RECYTUBE reports from years 1998–1999 (CREED 1998a–d, 1999a–c).

The areas for CRT utilisation for glazes, tableware products and construction blocks were found to be feasible for further study and industrial-scale production. Papers I–IV summarize the experimental work carried out in the following applications:

- ceramic applications: high-fired glaze, low-fired glaze
- glass application on hollow-ware products

Test series related to utilisation of CRT glass in forming of glass tiles and using CRT glass as a coating material are described in the Chapter 4.2.2. Test series.

The test series on the properties of CRT glasses, such as melting (Paper III) and sintering properties (Paper IV) and finding the possible applications for EOL CRT glass use, were carried out on laboratory scale at UIAH and at Åbo Akademi University, Department of Inorganic Chemistry. Laboratory-scale test series for various application areas were carried out at the University of Art and Design Helsinki. The most feasible applications from the laboratory scale experiments were chosen for industrial-scale testing. These tests were performed in Finnish ceramic and glass industry. Test series carried out 2001–2003 are discussed in detail in the publication "KIMOKELA- Kierrätetty monitorilasi keramiikka- ja lasiteollisuuden raaka-aineeksi" (in Finnish), (Keramiikka- ja lasitehteen koulutusohjelman tutkimusjulkaisuja No. 1, 2003, ISBN 951-558-117-6) University of Art and Design Helsinki, 2003.

Technical analysis was performed at Åbo Akademi University (Paper II, Paper IV), Glass Research Institute GLAFO (Paper IV) in Sweden, Stazione sperimentale del Vetro SSV (Paper I) in Italy, in the laboratories of Arabia ceramic factory (Paper II and Paper III) and of Schott Glass (Paper I) in Germany.



Photo 6. Test melting of Cathode Ray Tube glass at University of Art and Design Helsinki  
Photo: Satu Typpö.

## 4.2. Experimental Materials

Test materials for the experimental series were collected in many steps. The first lot, mixed panels collected from Germany and France, was used to the first preliminary test series, when studying possible open-loop application areas for CRT utilisation. The dismantling and purification processes were under development at this phase of the study, thus the degree of the cleaning was not adapted for open-loop applications, e.g. glass material contained around 8 wt-% lead oxide. There are two important sources of lead in this lot. Black and white devices may contain lead oxide in panel part. Additionally, no collection programmes of post-consumer electrical devices were in use, which resulted in recycling of very old devices and in a non-representative chemical composition. Batch number 1 contained 11.10 wt-% of iron impurities, of which source is likely to be external. With developed cleaning and crushing processes the level of iron impurities decreased to the level the source of which is internal.

The preliminary tests were continued with colour panel materials that had been found to have most suitable chemical composition for most of the possible applications in ceramic and glass industry. These materials were collected in Central Europe.

In the preliminary test series for low-fired glazes a lot prepared from post-consumer glass collected for closed-loop use of CRT production was applied. At this phase of the study, the collection procedure Finland was not complete yet.

For the latest tests and trials in the industrial-scale testing, the recycled CRT glasses were collected from Western Finland in years 2001–2002. The monitors were dismantled by using hot-wire technique and the coatings were removed by vacuum cleaning. The glass parts were separated to five different categories as follows:

- 1) colour PC panel glass
- 2) colour TV panel glass
- 3) mixed colour panel glass (TV & PC)
- 4) funnel glass
- 5) mixed glass (containing e.g. black & white CRT's)

Table 10. Analysed chemical compositions (wt-%) of experimental materials

1. Mixed panels, material collected from France and Germany in year 1997,
2. Material collected from Middle Europe,
3. Material from Europe collected for closed-loop use in year 2001,
- 4.–6. Colour panel glasses collected from Western Finland in 2001–2002 .

Oxide	Batch 1. wt-%	Batch 2. wt-%	Batch 3. wt-%	Batch 4. Colour PC panel wt-%	Batch 5. Colour TV panel wt-%	Batch 6. Mix colour panels wt-%
SiO <sub>2</sub>	58.8	59.71	62.08	60.3	61.6	61.4
Al <sub>2</sub> O <sub>3</sub>	6.10	2.29	2.97	2.37	3.26	3.17
Fe <sub>2</sub> O <sub>3</sub>	11.10	0.093	0.074	0.22	0.058	0.058
CaO	0.39	2.84	2.08	0.96	2.30	2.14
MgO	2.03	1.13	1.13	0.19	1.05	0.99
PbO	7.73	0.21	0.15	0.011	0.32	0.060
Na <sub>2</sub> O	7.60	8.26	8.17	8.36	8.57	8.45
K <sub>2</sub> O	2.00	7.73	6.94	7.55	7.36	7.11
TiO <sub>2</sub>	0.70	-	0.30	0.39	0.32	0.33
BaO	1.05	14.78	11.86	8.87	10.52	10.51
SrO	0.30	1.29	2.44	9.25	3.81	4.28
ZnO	0.60	0.007	0.08	0.23	0.08	0.12
As <sub>2</sub> O <sub>3</sub>	0.18	0.072	0.02	0.03	0.11	0.08
Sb <sub>2</sub> O <sub>3</sub>	0.10	0.61	0.39	0.44	0.57	0.62
CeO <sub>2</sub>	0.19	0.23	0.19	-	-	-

Categories 1–3, i.e. the lead-free panel glasses, were used as test materials for ceramic and glass applications. Beside the overall suitability for the selected application areas, the focus was on studying whether the differences in the chemical compositions of these three glass categories originating from the most common colour devices has an affect in specific application (Papers III and IV). For certain glass making processes, such as sintering, compositional variations in glass categories 1–3 should not be significant.

Photo 7.  
Collection of PCs for recycling.



Photo 8.  
The diameter of the cathode ray tubes varies according to its origin.



### 4.3. Processing of Experimental Materials

Collected post consumer devices were sorted, dismantled, their panel and funnel parts separated and coatings on separated glass parts removed. Glass materials were crushed and sieved according to the requirements of raw material quality for the application areas tested. Three different particle size fractions were used:

- 1) coarse: particle size 4–12 mm
- 2) medium: particle size 1–3 mm
- 3) fine: particle size below 1 mm

Glass lots were crushed both with jaw and centrifugal crusher in order to evaluate the proportions of the different particle size fractions formed with these techniques. The screening tests resulted in varying amounts of particle size fractions. The amount of fine size fractions needed for ceramic applications (sieve below 0.75) was 34.2 wt-% when using jaw crusher and 25,6 wt-% in case

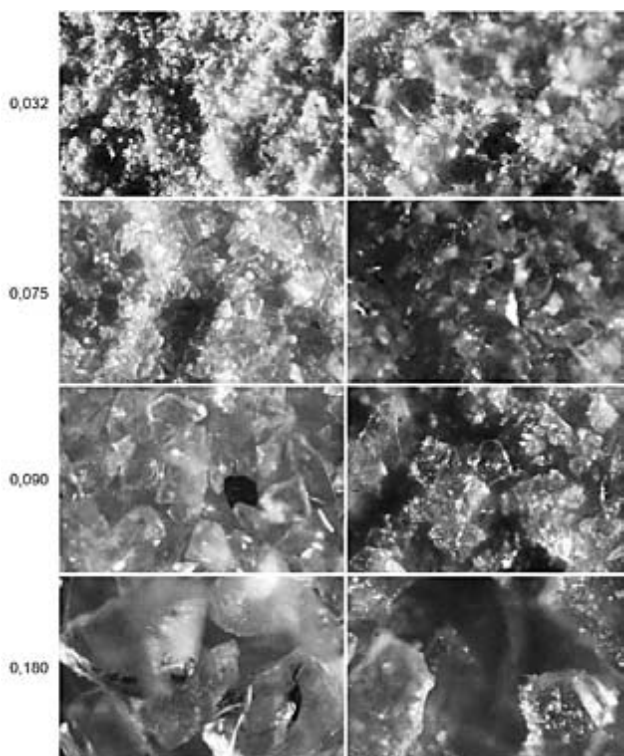


Photo 9.  
Recycled panel glass crushed  
with jaw and centrifugal  
crushing techniques.  
Microscope picture  
(magnification 40x) of the screened  
CRT glass particles. On the left,  
glass processed with centrifugal  
and on the right, jaw crusher  
(sieve sizes from the top  
0.032, 0.075, 0.090 and 0.180).



centrifugal crusher was used. The crushing technique also affected to the shape of the formed particles (see Photo 9.). The particles from the jaw crushing process have sharper edges and also may contain longer particles than glass material been through centrifugal crushing.

The chemical compositions of batches were analysed, c.f. Table 10. The thermal behaviour of experimental materials (PC, TV and mixed colour panel glasses) was analysed by heating microscope (Misura 3.0, Expert System) in the temperature range 500–1200 °C. Paper IV further describes the thermal behaviour of the experimental glasses.

#### **4.4. Test series**

Papers I–IV summarise the experimental work carried out for ceramic applications: high-fired glaze, low-fired glaze and for glass application, hollow-ware products. Additionally, further studies after laboratory-scale tests included the manufacturing of glass tiles. Glass tiles have been manufactured from recycled container glass according to the technology invented in Finland in the 1990's. The tiles, containing roughly 95% recycled glass, are manufactured by sintering process. The crushed and sieved glass is mixed with additives. The batch is led to a mould and the shape is formed with vibration casting. Dried tiles are fired to a according to a certain time-temperature profile to reach the temperature around the softening point of the glass. These tiles are used in various architectural structures both for interiors and exteriors.

##### **4.4.1. Production of Glass Tiles**

The test series were carried out in two phases: on laboratory scale the suitability of material to the forming and firing processes was tested. Test samples were made out of different proportion of particle size fractions, mixed according to three proportions. Porosity of tiles is crucial to the mechanical properties. It was measured from tiles fired at the temperature gradient 695–800°C with 10°C intervals.

For the laboratory-scale testing, mix panel glass composition, c.f. Table 10, glass batch 6, was used. Batches for glass tiles were produced by mixing various proportions of particle fractions, c.f. Table 11. The batches were mixed with additives, i.e. binders and water, dosed and cast into moulds with vibro-set on a pressing table. After casting, the tiles were moved to a dryer where the pieces were warmed up to achieve fast drying and bonding reaction of the materials. Dried tiles were taken out from the mould and moved to a firing kiln.

Table 11. The different particle size materials were mixed with proportions listed below.

	<b>Coarse</b> 4-12 mm wt-%	<b>Medium</b> 1-3 mm wt-%	<b>Fine</b> <180 mesh wt-%
Batch 1	30	50	20
Batch 2	50	30	20
Batch 3	70	20	10



Photo 10. Photo of gradient-fired test samples for glass tiles. Test samples with three different batches containing various particle size fractions were fired in the temperature range 695–800°C. Photo: Kirsti Taiviola.

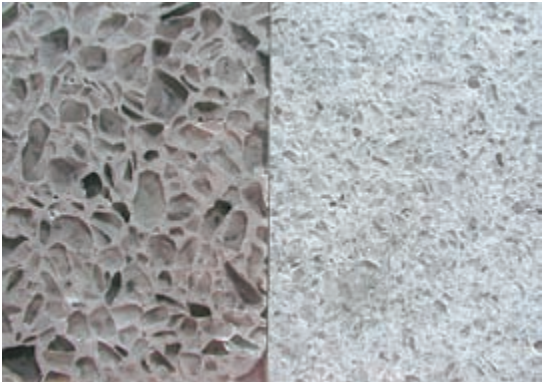


Photo 11.  
Photo of glass tiles (15 x 10 cm) made in laboratory. The colour hue of glass tiles is affected by the proportions of different particle size fractions in the batch.



A gradient firing was performed to find out the optimal sintering temperature for each experimental batch. The porosity of fired construction blocks was tested with standard testing method used by glass tile manufacturer. CRT glass blocks fired within the temperature range 680–740°C gave the same porosity as the reference, industrially manufactured container glass blocks fired at 900°C. The firing temperature was found to influence the porosity more than the weight ratio between the different particle fractions. However, the green packing density and thus the green strength varied between the different batches. It was found that the grey hue, typical to CRT panel glass, could be adjusted by the relative amount of coarse and fine particles, giving grey and whitish hues respectively (see Photo 11).

Test series with three batches were repeated on industrial scale, where glass tiles size 40x45 cm was produced. After sintering process, the tiles were polished.

As the porosity is one of the determining factors for frost resistance, it can be assumed that the CRT-glass blocks fired at this temperature range show a good frost resistance. However, no long-term tests were carried out to verify this.

#### 4.4.2. CRT Glass as a Coating Material for Glass Tiles

Typically, CRT panel glass has a lower softening point than container glass. The lower sintering point enables the use finely-ground CRT-glass as coating material for container-glass based tiles and the use of only one firing for finishing the surface, too.

Recycled CRT glass with particle size less than 180 mesh was used for glazing the container glass based tiles. The glazes contained 95 wt-% of recycled glass material with 5 wt-% of additives. Additives were used to adjust rheology, green strength and thermal expansion of coating.

Batches weighing 200 grams were ball-milled in water for two hours. After milling, the glazes were sieved and a suitable weight/litre ratio was adjusted in order to achieve a suitable density for spraying. The glazed glass tiles were fired with the same firing parameters both in an electric laboratory furnace and an industrial gas-fired kiln, c.f. Table 12.

Table 12. Firing parameters of container glass tiles coated with CRT glaze.  
Total firing time was 7 hours.

step	°C/h	Temperature °C	Soaking time min.
1.	300	830	5
2.	600	560	-
3.	100	500	-
4.	50	390	-
5.	300	80	-

The results indicate that the colour is rather uniform for glazes fired in electric furnace, while glazes fired in the gas-fired industrial kiln have some dark spots in their surface. The typical green colour of the glass tiles made out of container glass was more intense in glazed tiles fired in electric furnace. Surface quality and the appearance of the glazes met the requirements. The few pinholes in the surface could be avoided e.g. by using glazing methods, such as dry glazing that are more suitable for slightly uneven surface of the glass tiles.

## 5. Results

The results for these industrial application areas show EOL CRT colour panel glass to be a suitable raw material for ceramic glazes, both for low-fired (firing temperature 1020°C) and high-fired (firing temperature 1260 °C) ceramics. In glass industry, industrial-scale melting tests were performed with 100% recycled CRT colour PC panel glass and formed with different production techniques: blowing, casting and centrifugal casting. Both melting and forming processes as well the quality of formed products were found to be good. Recycled CRT glass was found to be a suitable material for manufacturing construction blocks containing 95 wt-% of CRT glass.

### 5.1. Ceramic Applications

The secondary raw material originating from the recycling and purification of end-of-life cathode ray tube glasses is a valuable raw material, especially in applications in which homogenous silicate compositions are desired. In ceramics, homogenous raw materials with a softening point suitable for a specific firing range are used especially in glazes.

#### 5.1.1. High-Fired Glaze

Glaze manufacture is a complicated industrial process, where several aspects of raw materials used should be taken into consideration. As a consequence, in this study CRT glass was tested as a raw material substitute to feldspar because of similarities in their compositions. A conventional glaze containing feldspar was used as a reference in the tests.

No marked differences in the glazing or firing behaviour of the experimental glazes and the reference glaze could be observed. However, the experimental glazes with the addition of glass cullet contained less non-molten residual quartz

after firing than the reference glaze. Whether this difference depends on the low softening and melting of the glass and thus earlier dissolution of the raw material quartz, cannot be deduced from these experiments only. The presence of quartz in the glaze surface is known to decrease the hardness of the glaze. Thus, the elimination of some free quartz from the glazes by introducing a homogeneous material, glass cullet, is likely to improve the mechanical and long-term stability of the glaze.

The content of colouring agents in the glass cullet from the cathode ray tubes is so low that they should not impart any colour hues in the glaze. However, the content of heavy metals, especially barium oxide is relatively high and the possible leaching of the barium should always be tested. So far, there are no regulations of maximum allowed leaching of barium from tableware ceramics. The tests indicate that the amount of barium leached from a tableware glaze containing 2.14% barium oxide is very low.

The results indicate that glass cullet from the end-of-life cathode ray tubes can be used as a raw material in glazes for tableware ceramics, i.e. products strictly controlled by legislation and by consumers. Since the recycled material shows applicable behaviour in such a demanding application as tableware glazes, its use in some other ceramic applications would also be possible. However, larger quantities of recycled CRT glass could be easily used to building ceramics, e.g. to tile glazes.

#### 5.1.2. Low-Fired Glaze

Experimental glazes containing 86–96% of cleaned and crushed EOL CRT glasses (TV, PC and mixed glass), were prepared and analysed after firing. The firing properties of the glazes and the surface properties of the final glaze surfaces were measured. Both the measured values and visual appearance of the experimental glazes indicate that CRT glasses can be used as a glaze material for low-fired ceramics.

No clear differences between the different glass sources – TV, PC and mixed glass – could be found. However, the glaze containing PC colour panel glass was most stable when the entire manufacture process was taken into account. Out of

the three clay bodies used in the test series, Danish and German earthenware were found to be more tolerant to the changes in the thickness of the glaze. On the test samples made out of Finnish earthenware, a thick glaze tended to develop hairline cracks more easily than when applied to the two other clay bodies.

The suitability of the experimental composition for coloured glaze was tested by adding seven different ceramic pigments to the glaze suspension. The results showed that glaze body is suitable to colouring purposes. To some extent, the colour hue depends on the chemical composition of the CRT-containing glazes. Compared to the lead-containing reference glaze, the experimental glazes containing CRT glass did not have the same gloss. The importance of lead oxide for the gloss and colouring of low-fired glazes has been reported in other studies, too (Hortling and Jokinen 2001).

## **5.2. Applications in Glass Manufacture**

In glass industry, the suitability of recycled CRT panel glasses to be utilised as a raw material for tableware and decorative ware manufacture was tested. Glass tiles were produced with sintering technique. Additionally, the suitability of CRT glass to be used a coating material for glass tiles made out of container glass was tested.

### **5.2.1. Tableware Glass**

Results from laboratory scale experiments indicated that recycled CRT panel glass could be a potential foreign cullet for small and medium-sized glass manufacture. Industrial-scale tests were performed by melting the glass batches in 40-kilos crucibles. A batch consisting of 100% recycled CRT colour PC panel glass was used in the industrial melting. Various products were formed using different production techniques: blowing, casting and centrifugal casting. The overall melting properties of the batch were satisfactory. One observed difference to the commercial tableware glass used as the reference was a few cords in some experimental glasses. Also the working properties of the glass were satisfactory as also could be presumed from the only minor differences in the calculated viscosities

of the reference and experimental glass (Table 6). The industrial-scale experiments indicate that recycled CRT cullet can be formed with various forming methods typically applied in small and medium sized glass industry producing tableware.

The tableware products made from the glasses melted in industrial furnace were tested for chemical durability by washing tests (500 and 1000 washing) without any failure. Also leaching tests performed according to a standard method indicate that recycled CRT glass can be used as a raw material for manufacturing of tableware products.

The use of CRT cullet, because of its low softening point, offers a possibility to operate the glass melting furnace at lower temperatures. This extends its lifespan and reduces the need for maintenance and expensive replacement.

#### 5.2.2. Glass Tiles

According to the technique invented in the 1990s in Finland, experiments of using CRT glass in the manufacture of glass tiles were carried out. Various proportions of different particle fractions were tested for tiles manufactured on laboratory scale. The batches were mixed with additives, i.e. binders and water, dosed and cast into moulds with vibro-set on a pressing table. After casting, the tiles were dried, taken out from the mould and moved to firing kiln. A gradient firing from 650–850°C with 10°C intervals was performed to determine the optimal sintering temperature.

The porosity of fired construction blocks was tested with a standard testing method. CRT glass blocks fired within the temperature range 680–740°C gave the same porosity as the reference, industrially manufactured container glass blocks fired at 900°C. As the porosity is one of the determining factors for frost resistance, it can be assumed that the CRT-glass blocks fired at this temperature range show a good frost resistance. The colour of CRT glass offers the possibility to achieve an aesthetically interesting solution to the product that can be used in different architectural structures. When used as a crushed glass of different particle sizes, special effects with partial transparency of glass tiles can be achieved.

Thus, glass tile production offers a feasible solution to use large amounts of CRT glass in open-loop recycling. As tiles are manufactured by sintering the

particle fractions at temperatures that are several hundred degrees lower than typical glass melting temperatures, minor compositional changes in purified EOL CRT glass do not adversely affect the processing or final properties of the tile. Compared to container glass, the CRT glass has lower viscosity. For this reason, sintering at lower temperatures is possible than presently used in industrial glass tile manufacturing.

Finely-ground CRT-panel can be utilised in glazing glass tiles produced from container glass because of its lower softening point. Recycled CRT glass of particle size less than 180 mesh was used for the glazes. The glazes were mixed of 95 wt-% of glass and 5 wt-% of additives adjusting their rheology, green strength and thermal expansion.

Glaze batches were ball-milled, sieved and a suitable weight/litre ratio was adjusted in order to achieve a suitable density for spraying. The glazed glass tiles were fired with the same firing parameters both in an electric laboratory furnace and an industrial gas-fired kiln. The results indicate that the colour is rather uniform for glazes fired in the electric furnace, while glazes fired in the gas-fired industrial kiln show some dark spots in their surface. The typical green colour of the glass tiles made out of container glass was more intense in glazed tiles fired in electric furnace. Surface quality and the appearance of the glazes were desired. The few pinholes in the surface could be avoided e.g. by glazing methods such as dry glazing more suitable for slightly uneven surface of the glass tiles.

## 6. Concluding Remarks

In high-temperature applications, CRT glasses were used without any marked deterioration of product quality or disturbances in processing. While processing, CRT glasses were found to allow to decrease processing temperatures, which translates into possibility of saving energy. Reduced energy consumption allows significant environmental benefits: carbon oxide emissions from the combustion of fuel and emissions from raw materials can be reduced. Reduction of thermal NO<sub>x</sub> emissions is possible due to the reduction of combustion energy. Lowered operation temperatures reduce the corrosion of refractory materials, thus extending the lifecycle of machinery used in high-temperature productions.

Considering materials, environmental benefits are dual: the amount of waste material and the use of virgin raw materials can be reduced, which means reducing the need of transporting or storing them. This will protect natural resources for future generations.

Possible disadvantages in utilisation of CRT glass materials in ceramic and glass industry are risks of potential contamination, when material dismantling or/and cleaning has not been successful enough to meet the raw material requirements of the end-user. Processing of glass material has to be planned carefully, e.g. glass cullet as a hard and abrasive material can bring along some impurities, like iron from crushing machinery. This can be avoided by using materials that come into contact with glass gross that are as harmless to the end-user's process as possible. In case iron impurities are likely, magnetic screening of the material can be added to the sieving process. In glass industry possible disadvantages in using recycled glass are potential glass defects, like cords as well as viscous and redox issues. Impurities can also cause colouring of glass.

Limitations for the introducing recycled material to the industrial processes that are due to changes in chemical composition of materials, can be overcome by good dismantling techniques and by controlling the lot sizes. Big lots give better homogeneity of the recycled material. Moreover, homogeneity from lot to lot will be better, when a large amount of material balances the differences in chemical composition, caused by glass coming from different producers and dates of production.



## 7. Future Challenges

The application areas for CRT utilisation in ceramic and glass industry can hopefully be a starting point for wider research in this area. In ceramic and glass industry, there is a wide range of various production processes and end products ranging from bulk products, such as construction materials e.g. bricks and tiles, to high-technology applications, such as reactive glass materials. These could open up various new areas for studying utilisation of CRT glass as a secondary raw material. Preliminary tests carried out in this study, such as the use of CRT glass in the clay body, would be an interesting area for further study. An important consideration is that each manufacturing process in ceramic and glass industry has its own requirements for secondary raw materials. Processes are sensitive to changes in raw material composition. Thus, every process requires a specific study before a new secondary raw material can be utilised.

Local variations, such as market situation and politics, have an important effect on the reuse materials. Legislation is one of the key factors in enhancing the use of secondary raw materials. Beside legislation, close co-operation between the manufacturers, recyclers and end-users of the recycled material is necessary. It is needed both to enhance waste prevention and to maximise the quantity of suitable material for recovery and to minimise the loss of materials in cases where production of waste cannot be prevented.

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# Appendix

## List of abbreviations

ASR     Alkali Silica Reaction

BFR     Brominated Flame Retardants

CRT     Cathode Ray Tube

EEE     Electrical and Electronic Equipments

EOL     End-of-Life

IPP     Integrated Product Policy

LCD     Liquid Crystal Display

PC     Personal Computer

RoHS-directive

Directive 2002/95/EC of the European Parliament and of the Council on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment

UIAH    University of Art and Design Helsinki

XRF     X-ray Fluorescence Spectroscopy

WEEE   Waste from Electrical and Electronic Equipment

WEEE-directive

Directive 2002/96/EC of the European Parliament and of the Council on Waste Electrical and Electronic equipment



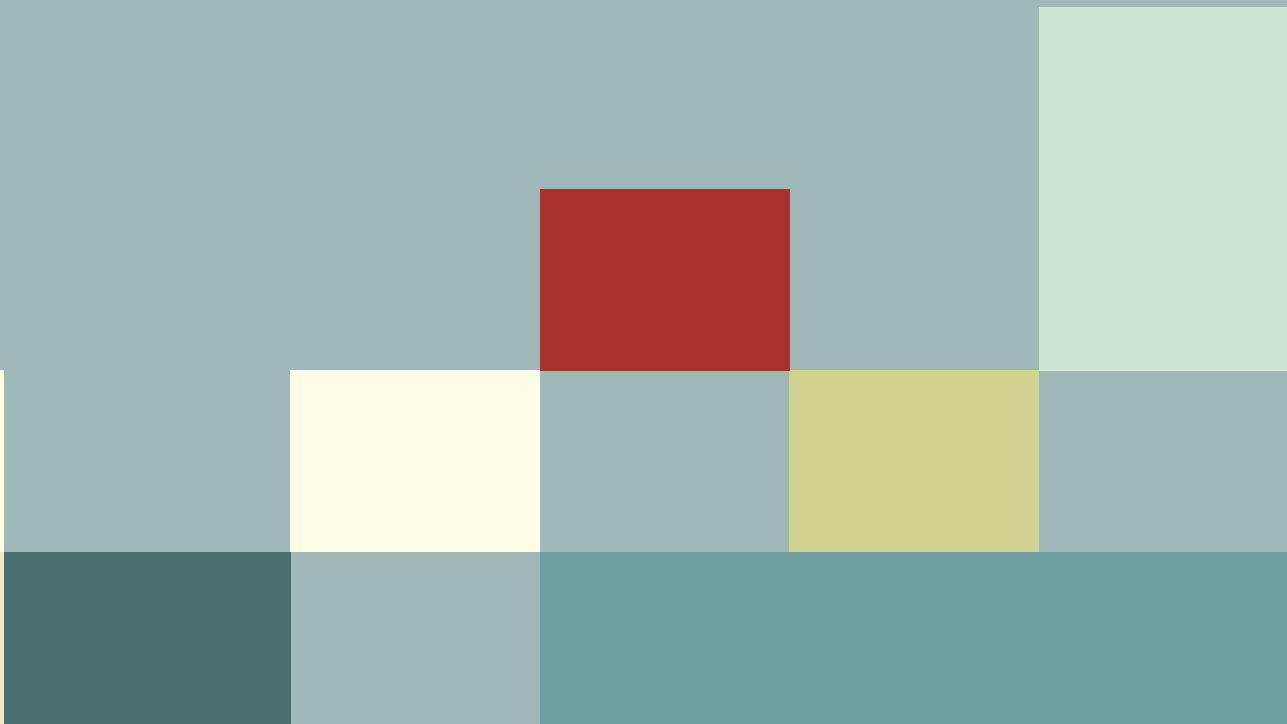
# Part II

## Article I



**Raija Siikamäki, Eckart Döring, Jorma Manninen**

Closed-loop and Open-loop  
Applications for End-of-Life  
Cathode Ray Tube Glass Recycling





# CLOSED-LOOP AND OPEN-LOOP APPLICATIONS FOR END-OF-LIFE CATHODE-RAY-TUBE GLASS RECYCLING

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**Abstract:** Both legislative initiatives and collection programs, currently existing and being developed, will increase the amount of End-of-Life (EOL) Cathode Ray Tube (CRT) glass coming to the recycling market. This glass material from PCs and TV sets can be a valuable material, but at the same time problematic for a number of reasons, e.g. because of the need for multistage treatment including separation, cleaning and crushing, and because of a wide range of different chemical compositions. To develop industrial, cost-efficient applications for the use of EOL CRT glass material is a big challenge. This study summarises closed-loop applications and open-loop applications tested for Finnish ceramic and glass industry for EOL CRT glass and requirements for CRT dismantling and treatment processes. In order to be able to produce a high-quality secondary raw material, the presence of harmful materials that CRT's contain has to be taken into account in dismantling and treatment processes as well as in occupational and environmental safety.

## 1. INTRODUCTION

The Decision of the Commission of the European Communities on January 16, 2001 amending decision 200/532/EC as regards the list of wastes was published on February 16, 2001 in the Official Journal of the European Communities [1]. According to the amended list of wastes discarded electrical and electronic equipment containing hazardous components such as glass from cathode ray tubes are classified as hazardous waste.

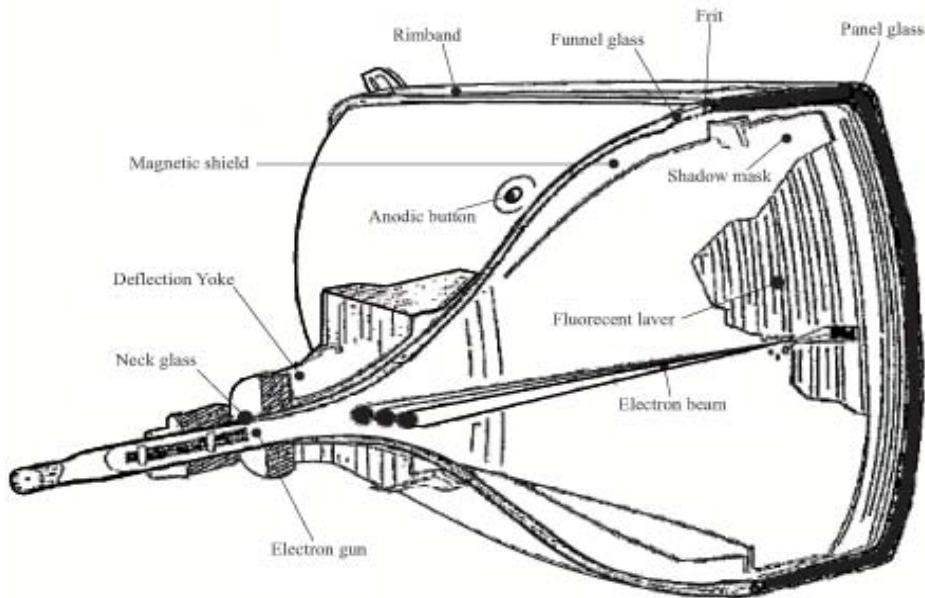
According to the Proposal for a Directive of the European Parliament and of the Council on waste electrical and electronic equipment (WEEE) the cathode ray tubes have to be removed from separately collected WEEE for selective treatment [2]. The selective treatment means that the fluorescent coating has to be removed from the cathode ray tubes. According to the proposal for WEEE falling under categories IT & Telecommunication equipment and Consumer equipment the rate of recovery shall be increased to a minimum of 75% by an average weight per appliance, and component, material and substance re-use and recycling shall be increased to a minimum of 65% by an average weight per appliance. In practise this means that cathode ray tube glass must be recycled to reach the recycling target for discarded televisions and monitors. The recycling target must be reached as early as by the

end of 2005. For this reason, the closed-loop recycling process of cathode ray tube glass should be maximised and new ideas should be developed to improve open-loop recycling for cathode ray tube glass.

In developing closed-loop recycling, i.e. the use of EOL CRT into new CRT's, glass makers have made remarkable progress: at the moment more than 30% of EOL CRT glass can be used in the funnel glass and at least 15% in the panel glass production. For open-loop recycling, ceramic and glass production are the fields of industry in which it is possible to utilise the valuable properties of lead-free EOL CRT panel glass to the full. It is a valuable silicate raw material. In many applications the re-use of this material can also reduce the specific energy consumption. In the production of ceramics, CRT panel glass can be used as a substitute for virgin raw materials in glazes. In the production of glass, CRT glass can be utilised as substitute for cullets or some production processes can be fully based on the use of this secondary raw material.

## 2. COMPONENTS OF A CATHODE RAY TUBE

A typical colour CRT is shown in fig. 1. CRT consists of five different glass types:



**Figure 1.** The components of a typical colour CRT.

- the panel glass (the front part of cathode ray tube)
- the funnel (the backside)
- the neck (contains electronic gun)
- the stud with the electrical contacts
- the glass solder "frit" which connects the panel and the funnel glass.

The main glass types are panel, which makes up about 2/3 of the total mass of the CRT, and funnel glass, which corresponds to 1/3. With the exception of panel, the content of lead oxide of these glass types varies from 10 to 85%.

The CRT also contains many non-glassy parts: the metallic shielding (ferromagnetic), the shadow mask (ferromagnetic) and the electron gun (non-magnetic). The mask is assembled with 4 metallic pins (ferromagnetic) which are molten into the glass and the acceleration voltage is applied through a metallic button (ferromagnetic) molten into the funnel glass.

The glass itself is covered with different functional layers:

- the fluorescent layer on the panel glass (consists of zinc sulphides and rare earth oxides)
- some amounts of cadmium in the fluorescent layer of old CRT's

- an aluminium plating on the backside of the fluorescent layer
- a graphite layer on the outside of the funnel
- an iron oxide layer on the inside of the funnel

In principle there is no difference between CRT glass of TV sets and computer monitors. Thus monochromatic and black & white tubes differ from colour monitors because they consist of only one glass type containing about 3% of lead also in the panel section.

## 2. DISMANTLING AND CLEANING OF CRT'S

The EOL CRT glass can not be used without any treatment. The CRT contains a lot of contamination and foreign materials and the glass is covered with functional layers. These non-glassy materials and coatings have to be removed by several sorting and cleaning steps.

This treatment process can be split into two different levels: the first level covers mainly the separation of the different glass types and the removal of all foreign materials.

The second part of the treatment covers mainly the cleaning of the glass from the layers, homogenisation and the adjustment of the final grain size distribution. The homogeneity of the final material is one of the key criteria for the ability to reuse the material. For instance, when using 30% addition of EOL cullets, a variation of 1% for one oxide in the glass lot will result in a

The properties of the secondary raw material are mainly defined at the dismantling and cleaning stage. Therefore, more advanced and more expensive equipment is needed, higher investments and trained personnel will be necessary. Very few centralised plants can cater for this.

Selective treatment of discarded WEEE requires also new innovations to ensure safe working environment for the dismantlers and process supervisors. They are also necessary to reach high recycling targets. Recycling is feasible only if hazardous components are removed and metals, plastics and glass, etc. can be sorted either manually or automatically to raw materials with the homogeneity needed.

Manual disassembly and mechanical treatment expose employees to working hazards such as dust which has accumulated in the equipment before discarding. The dust is released when the equipment is dismantled and therefore the ventilation system must be efficient enough to collect the dust and to filtrate the hazardous particles. It is possible to design the ventilation system so that the employees do not necessarily need respiratory protective equipment. Mechanical treatment process equipment can be encapsulated so that dust can be collected and filtrated efficiently to reduce emissions to the ambient air to a minimum.

change of 0.3% in the final glass. This will change the physical properties more than the specification would cover and would cause all molten glass for about one week to be rejected. The homogeneity has to be better than 0.2% variation for the most important oxides, which can only be achieved by special treatment.

Glass dust is dangerous to the lungs and cathode ray tube glass recycling exposes employees to hazardous substances such as fluorescent powder and glass dust containing lead. The concept of a dust-free atmosphere in recycling and waste management is not an easy target to reach without applying new ideas and investing money and effort in the environmental design of the treatment processes. However, it is a necessity, if we want to guarantee a safe working environment and high-quality raw material from dismantling and cleaning processes.

### 3. PROPERTIES OF CRT GLASSES

The CRT glass types are special glasses. They are characterised by physical properties shown in table 1. These properties are reached through the specified chemical composition. They have been changed several times, mainly to increase the safety of the consumers. Additionally, technical demands in the production of CRT's have caused many changes. As a result, there are for example about 50 different TV-glass compositions on the market at the moment. Tables 3 and 4 show the calculated variations of funnel and panel glass compositions between years 1997-2001.

The current compositions of panel and funnel glass contain the same oxides as the old compositions, but their ratios vary.

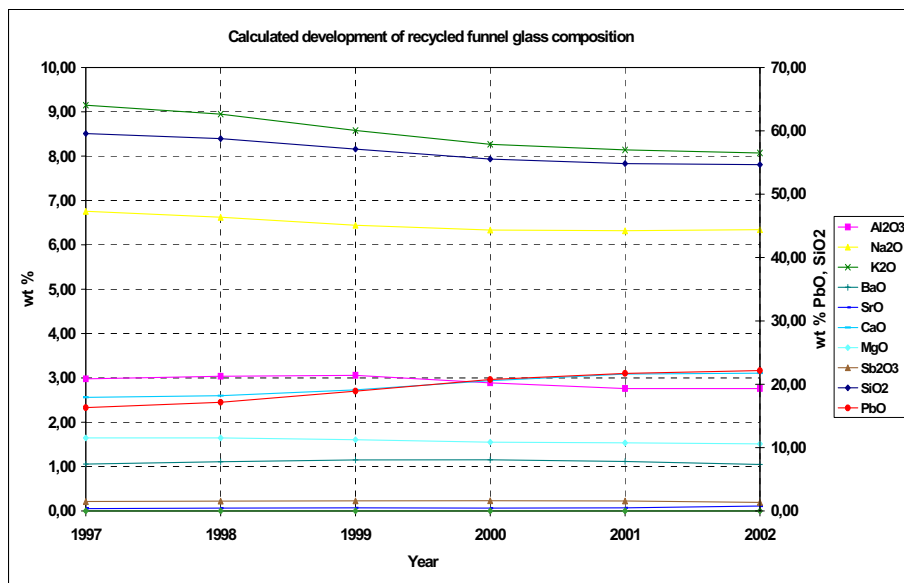
**Table 1.** Physical properties of panel and funnel glass

Parameter	Panel glass	Funnel glass
Linear expansion coefficient	10 E-6/K	9,8 E-6/K
TK 100	ca. 290 °C	ca. 330 °C
Density	2.78 g/cm <sup>3</sup>	3.0 g/cm <sup>3</sup>
Working point	ca. 1000 °C	ca. 960 °C
Transformation temperature	ca. 500 °C	ca. 460 °C
X-Ray absorption	>28 cm-1	>65 cm-1

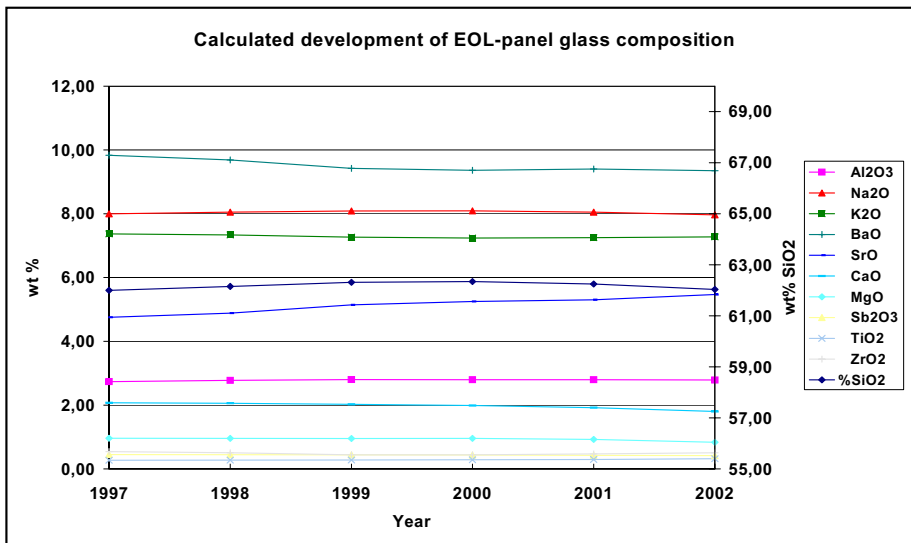
**Table 2.** Range of chemical composition of panel and funnel glass

%	Panel glass			Funnel glass		
Oxide	<i>Min</i>	<i>Max</i>	<i>Variation</i>	<i>Min</i>	<i>Max</i>	<i>Variation</i>
SiO <sub>2</sub>	58.85	65.40	6.55	51.19	63.45	12.26
Al <sub>2</sub> O <sub>3</sub>	1.20	3.70	2.50	1.10	5.00	3.90
Na <sub>2</sub> O	6.15	9.80	3.65	5.25	8.05	2.80
K <sub>2</sub> O	6.00	8.95	2.95	7.15	10.30	3.15
Li <sub>2</sub> O	0.00	0.50	0.50			
F	0.00	0.83	0.83			
BaO	1.90	14.20	12.30	0.00	3.00	3.00
SrO	0.00	11.60	11.60	0.15	0.65	0.50
CaO	0.00	4.55	4.55	1.60	4.45	2.85
MgO	0.00	1.95	1.95	0.90	3.00	2.10
As <sub>2</sub> O <sub>3</sub>	0.00	0.30	0.30	0.00	0.15	0.15
Sb <sub>2</sub> O <sub>3</sub>	0.18	0.70	0.52	0.02	0.35	0.33
TiO <sub>2</sub>	0.00	0.60	0.60			
CeO <sub>2</sub>	0.00	0.55	0.55			
PbO	0.00	3.25	3.25	11.60	24.60	13.00
ZrO <sub>2</sub>	0.00	3.50	3.50	0.20	0.20	0.00
ZnO	0.00	0.65	0.65			
Fe <sub>2</sub> O <sub>3</sub>	0.03	0.07	0.04		fig. in weight-%	

**Table 3.** Calculated development of recycled funnel glass composition between years 1997-2002



**Table 4.** Calculated development of recycled panel glass composition between years 1997-2002



By taking random samples from a set of CRTs delivered from a recycler, it is found that the expectations calculated in tables 3 and 4 were correct. The whole spectrum of chemical compositions was found within these randomly taken samples (Table 5).

**Table 5.** Range of chemical compositions found in randomly taken samples of recycled panel glass.

Oxides	Min.	Max.	Standard deviation
Na <sub>2</sub> O	7.5	10.7	1.243894178
MgO	0.01	1.9	0.570631628
Al <sub>2</sub> O <sub>3</sub>	1.93	3.72	0.62910952
SiO <sub>2</sub>	59.9	63.6	1.411961885
K <sub>2</sub> O	6.66	7.93	0.408065466
CaO	0.12	4.45	1.208278264
TiO <sub>2</sub>	0	0.53	0.201334563
Fe <sub>2</sub> O <sub>3</sub>	0.04	0.09	0.018090681
ZnO	0	0.47	0.141234814
SrO	0.21	11.5	4.078396428
ZrO <sub>2</sub>	0.03	2.53	0.767479148
Sb <sub>2</sub> O <sub>3</sub>	0.32	0.51	0.069298432
BaO	5.54	13	2.286749711
CeO <sub>2</sub>	0.1	0.29	0.056219268
PbO	0	1.86	0.529545259
F	0	0.1	0

## 5. CLOSED-LOOP RECYCLING

Closed loop recycling is the reuse of a secondary raw material for the production of the same product as it was before; in this case TV funnel or panel glass. In principle the reuse of EOL glass is possible for the both funnel glass and panel glass production. Because of lower quality demands of funnel glass, the reuse started in the funnel glass production.

### 5.1 Closed-loop recycling of funnel glass

Different fractions of EOL glass are available on the recycling market: separated funnel glass, separated panel glass, monochrome glass and mixed glass from broken or crushed CRT's. Because there were no specific demands for separated glass in the past, the mixed glass fraction still is the dominating fraction on the market and well-separated fractions are not frequently available. All these fractions could be used in funnel glass production if the target composition of the new glass is adapted, which means that the composition contains barium oxide. If the new funnel glass contains enough BaO, mixed glass or panel glass can be added until the content of barium oxide is saturated by EOL glass without any change in the target composition and respectively without any change of the physical properties of the produced glass.

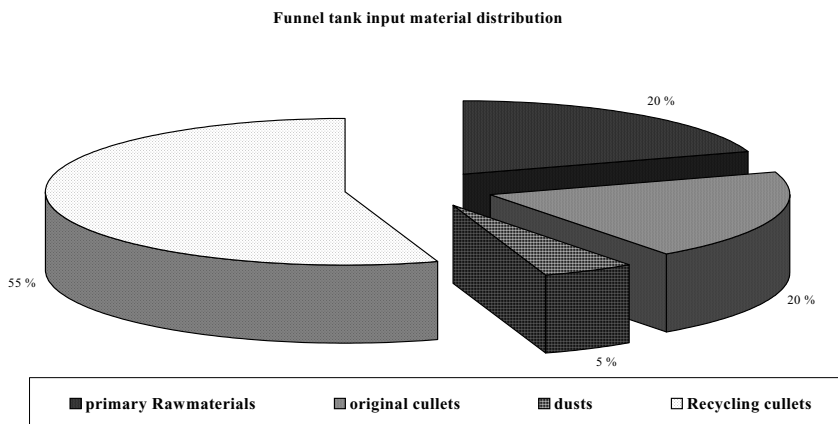
Due to the different contents of barium oxide coming from different input fractions, the limit for the possible addition depends on the type of EOL glass used.

For the funnel glass currently produced by Schott Glas the limitations are 6% of the melting capacity for panel glass addition and 25% for mixed glass. Glass from monochromatic CRT's has the same limitations as panel glass; a small amount could be accepted for the funnel production, but it reduces the usable amount of mixed glass due to the high content of barium oxide (12%). For the reuse of funnel glass in funnel glass production there is no chemical limitation for saturation of oxides.

Every glassmaker has to reuse his original cullets and other "wastes" from the glass production: slurries and dust for example from the waste gas treatment. Further, an amount of primary batch (10-20%) is needed to compensate the different chemical compositions of the old and the new glass. Taking into account all this, a possible distribution of input materials for the funnel tank is shown in figure 4.

The logistic limitation for the reuse of separated EOL funnel glass will be around 55% of the melting capacity of the funnel tank. In practice, in most cases a mixture of mixed glass and funnel glass will be used in the funnel tank to react on the distribution of fractions the market offers. In this case the highest recycling rate could be reached by using mixed glass as much as chemically possible together

**Table 6.** Distribution of material input in funnel tank



with separated funnel glass until the logistic limit would be reached for the sum of both fractions.

To be able to calculate the correction batch for the reuse of EOL it is important to know the properties of the secondary raw materials, in this case it is necessary to know the mean chemical composition of a lot. There are two possibilities to

reach this aim:

1. on-line analysis of any CRT or cullet,
2. homogenisation of a lot ( $\geq 500t$ ) while preparing and representative analyses afterwards.

The first way gives the exact result, but it is unpractical and expensive. Practice has shown the second correction method to be more feasible. The homogenisation of the material is a key to high recycling rates and has to be performed in both cases.

## 5.2. Closed-loop recycling of panel glass

Higher quality demands are set for panel glass than for funnel glass: beside the chemical composition two more properties have to remain stable in panel glass: the light transmission and the colour point. The colour point is a definition of the glass colour, transformed into a rectangular co-ordinate system. The specifications are very strict; e.g. the addition of ppm  $Cr_2O_3$  would make the glass rejected for some days. As there are different chemical compositions on the market, also four different colour points have been or are being produced. The transmission of the different panel glasses show a variation of 45%, ranging from 42% to 83%. Light transmission and colour point are controlled by the addition of colouring oxides. In the case of panel glass, NiO

and CoO are used. Also the contamination of raw materials will influence the content of colouring oxides. The optical properties depend on the reaction between colouring oxides and the glass matrix. Therefore, different additions of colouring oxides are necessary for each chemical composition of panel glass. To overcome



problems due to the variation range in chemical composition and optical properties, two approaches are theoretically possible:

1. determination of all properties for each CRT or cullet type and
2. homogenisation of a large lot and determination of the optical and chemical properties using representative samples.

To avoid browning of the panel glass due to electron irradiation the glass has to be lead free. Unfortunately panel and funnel are fixed by a glass frit containing 85% lead. Therefore, panel and funnel glass must be separated in such a way that no lead remains with the panel glass. Only a few separation techniques in Europe can meet these requirements: an optimized hot wire technique, a water-cooled diamond saw technique or a laser separation technique (under development). The possibility to use up to 15% of EOL panel glass in closed loop recycling has already been proven; higher recycling rates will be tested when there will be enough material available.

As for the funnel glass production, there will be two limitations for the reuse of panel glass in the closed loop: a chemical limitation defined by the contamination with colouring oxides due to the upgrading process and by homogeneity of the material. The other limitation will be a logistic limitation like for funnel glass; this limitation will be at about 40% of the melting capacity of a tank due to the internal recycling circuits and the need of primary raw material for compensation.

## 6. OPEN-LOOP RECYCLING

The application areas in which the valuable properties of EOL CRT glass can effectively be used are glass and ceramic production. Each production process in ceramic and glass industry has specific requirements for raw materials. The range in which the properties can vary is determined by the production process as well. A detailed description of production processes and quality of used raw materials is needed for each end-user.

The comparison between chemical compositions of different recycled glass materials and basic glass and ceramic raw materials shows similarities e.g. chemical compositions of feldspars and CRT panel glasses have mainly similar oxide compositions. Chemical compositions of the EOL CRT colour panel glass and two Finnish feldspars are listed in table 7. The basic oxide composition and thermal behaviour of EOL CRT panel glasses and glass material used e.g. in tableware production are comparable.

The cleaning and crushing processes and their quality control is essential for recycled

glass material utilisation in open-loop applications: only lead-free glass material can be utilized. The cost minimisation of the recycling cycle will have an important role also because of the relatively low cost of the main raw materials used in ceramic and glass production.

Beside the use in existing production processes another starting point for recycled glass material use is to start from the products: to design products where the recycled materials can produce added value. Such product groups are e.g. ceramic and glass ware for construction, interiors and tableware products.

**Table 7.** Chemical compositions of the EOL CRT colour panel glass and two Finnish feldspars. The feldspars are commercial raw materials supplied by SP Minerals Oy Ab [4]. The compositions are given in wt-%.

Oxide	Finnish flotation Feldspar	Finnish Alavus Feldspar	EOL Colour PC panel Analysed *
SiO <sub>2</sub>	67.2	72.0	60.3
Al <sub>2</sub> O <sub>3</sub>	18.3	15.7	2.37
Na <sub>2</sub> O	5.0	3.7	8.36
K <sub>2</sub> O	7.7	7.5	7.55
MgO	>0.03	>0.03	0.19
CaO	0.5	0.2	0.96
ZnO	-	-	0.23
Fe <sub>2</sub> O <sub>3</sub>	0.13	0.03	0.22
Density	2.59 g/cm <sup>3</sup>	2.61 g/cm <sup>3</sup>	2.72 g/cm <sup>3</sup>

\* + BaO 8.87, PbO 0.011, Sb<sub>2</sub>O<sub>3</sub> 0.44, ZnO 0.23, As<sub>2</sub>O<sub>3</sub> 0.03

### 6.1. Studied glass applications

The basic oxide composition and thermal behaviour of CRT colour panel glasses and glass material used in tableware production is comparable. An important advantage of using cullet is the lower energy consumption due to lower melting temperature of cullet when compared to use of batch. The melting time and the homogenisation of the glass materials are important factors as well the colour of glass.

#### 6.1.1. Tableware glass production

The working properties of glass material are of great importance for glass production. The viscosity-temperature -dependence of glass sets limits for use of different production techniques: e.g. a lower viscosity is needed in casting than in the blowing process. Table 4 shows temperature-viscosity comparison between PC and TV colour

panel glass and commercial tableware glass. The table shows that the differences in viscosity vs temperature and properties are relatively small and CRT panel glasses could be used in a similar manner to conventional glass material used in tableware

**Table 8.** Analysed chemical compositions of EOL CRT colour panel glasses and commercial tableware glass. Analysed compositions of EOL CRT are from test materials collected in Finland 2001-2002.

	CRT glass		commercial tableware glass
Oxide	colour PC panel analysed wt%	colour TV panel analysed wt%	analysed wt%
SiO <sub>2</sub>	60.3	61.6	69.0
Al <sub>2</sub> O <sub>3</sub>	2.37	3.26	0.37
Na <sub>2</sub> O	8.36	8.57	10.2
K <sub>2</sub> O	7.55	7.36	7.4
Li <sub>2</sub> O	-	-	0.19
MgO	0.19	1.05	0.035
CaO	0.96	2.30	3.6
ZnO	0.23	0.08	2.26
BaO	8.87	10.52	5.3
B <sub>2</sub> O <sub>3</sub>	-	-	1.23
Fe <sub>2</sub> O <sub>3</sub>	0.22	0.058	0.029
SrO	9.25	3.81	-
Sb <sub>2</sub> O <sub>5</sub>	0.44	0.57	-
As <sub>2</sub> O <sub>5</sub>	0.03	0.11	-
PbO	0.011	0.32	-
Sb <sub>2</sub> O <sub>3</sub>	-	-	0.2

production. From this starting point the test series for different tableware glass production methods was planned and carried out. The used test material was 100 % of colour PC panel. Tested production methods were blowing, centrifugal casting and conventional casting.

A production process similar to normal production was used. The behaviour of CRT glass was comparable to normal tableware glass with adjustment of working temperature.

Surface durability of the products was tested from the produced pieces with washing tests. The differences between the samples were followed in controls after 250, 500 and 1000 washings. The tableware products made out of CRT glass had a quality similar to the reference pieces after washing tests.

**Table 9.** Comparison of temperature-viscosity (calculation based on Lakatos model) and properties (according to Appen) with PC and TV colour panel glass to commercial tableware glass.

T/C	EOL CRT Colour PC panel dPas	EOL CRT Colour TV panel dPas	Commercial glass dPas
500	12.89	13.40	13.24
600	9.59	9.81	9.53
700	7.51	7.60	7.31
800	6.09	6.10	5.83
900	5.05	5.02	4.77
1000	4.25	4.20	3.98
1100	3.36	3.56	3.36
1200	3.13	3.05	2.87
1300	2.71	2.62	2.47
1400	2.36	2.27	2.13
1500	2.07	1.97	1.85
exp.	10.07 -06 1/K	10.20-06 1/K	99.70-07 1/K
density	2.5733 g/cm <sup>3</sup>	2.6269 g/cm <sup>3</sup>	2.555 g/cm <sup>3</sup>
refr. index	1.5155	1.5233	1.520



**Figure 2.** Products made from EOL colour panel glass with different production techniques (blown cylinder, centrifugal casted bowl and casted candleholder).

Tableware products having contact with food must have an excellent chemical durability. Leaching tests were performed with standard method (DIN 12111). The results showed that the 3<sup>rd</sup> hydrolytic glass had a chemical

durability corresponding to commercial tableware glass and there was no release of toxic elements.

#### 6.1.2. Production of construction blocks

Skerratt [3] has described the products, production process and properties of construction blocks by Innolasi Oy (Finland) with 95% of recycled package glass. The possibilities to utilise CRT glass in this process has been tested in laboratory scale.

The testing of EOL CRT glass use for making construction blocks is based on the process of determined particle size distribution of the glass cullet and vibration casting of the glass. Sintering of blocks after diamond cutting and polishing are shown in figure 3.



**Figure 3.** Construction blocks of 95% colour panel glasses. The variation in the colour hue has been achieved with different particle size distribution of the glass material.

Construction materials could utilise big amounts of EOL CRT glass material not only because of the scale of the production, but also because this application consisting only a small percentage of additives would give good possibilities for the reuse EOL CRT panel glass.

#### 6.2. Utilisation of CRT glass in glazes

Purified CRT glass cullet is a very valuable raw material for applications where homogeneous silicate compositions are needed. Additionally, CRT panel glass cullet contains barium, strontium and zirconium oxides, i.e. components that are often added to glazes because of their positive effect on glaze quality. The glass cullet could be described as a homogeneous alkali-alkaline-earth-silicate containing some alumina but relatively much barium oxide. If starting from crystalline raw materials such as sand and alkali carbonates, the formation and mixing of silicates to a homogenous material is a very energy-consuming

process. The homogeneous silicate glass cullet can be regarded as an energy effective raw material for ceramic applications.

Use of EOL CRT cullet as a substitute for feldspar for glaze in temperature area 1260 °C is described by Siikamäki & Hupa. [4]. A commercial tableware glaze with high quality requirements was chosen as a reference glaze. The properties of the experimental glazes containing 4.5, 9.0 or 14.5 wt-% of the CRT glass cullet were tested and compared to the industrially used reference glaze. No significant differences to reference glaze could be detected: the appearance and long-term chemical stability which were tested by a standard method of the glazes was fully comparable with the reference glaze.

In laboratory scale EOL CRT panel glasses as a glaze material for temperature area 1020 °C was tested. In this temperature strong fluxes, mainly lead oxide, are needed in order to make the glaze to melt. With a material already once molten - like glass - it is possible to achieve maturing of glaze without flux addition and a lead-free glaze becomes possible. In this temperature area, the clay material used is earthenware. Products made with this kind of production processes are e.g. bricks and some tableware products.

The aim was to utilize the maximum amount of EOL material and compensate the properties of glaze with additives. The raw quality of glaze, melting behaviour and quality of fired glaze has been tested. Laboratory-scale testes showed promising results and test series will be continued on industrial scale. Figure 4 shows some products glazed with test glazes made with 95-97 % of EOL colour panel glass and with coloured versions of this baseglaze.



**Figure 5.** Examples of products glazed with coloured versions of this the baseglaze with 95 % of EOL CRT colour panel glass

The content of colouring agents in the glass cullet

from CRT's is at such a level that they should not impart any colour hues in the glaze. However, the content of heavy metals, especially barium oxide is relatively high and the possible leaching of the barium should always be tested. At present, there are no regulations on maximum leaching of barium allowed in tableware ceramics.

## **7. FUTURE ASPECTS OF RECYCLING OF CRT GLASS**

Selective collection of discarded WEEE in general and equipment containing CRT glass in particular need new collection, packaging and transportation systems to ensure working safety of the employees of the waste management branch and to ensure availability of high-quality raw material from dismantling and cleaning processes. Discarded equipment has not been designed for collection and transportation without packaging and therefore, new innovative methods are needed for safe collection and transportation.

In the near future the re-use of EOL CRT glass will be increased. The logistics will become more and more important because of increasing amounts of this material. The costs for logistics as well as for the upgrading process will become more important to keep the process feasible. When using higher amounts of recycled cullets, requirements for raw material quality will become more strict: e.g. the material must be more homogenic because any variation of the properties of the EOL material will have more direct impact on the properties of the new material.

## **8. CONCLUSIONS**

In developing closed-loop recycling, glass makers have made remarkable progress: at the moment more than 35% of EOL CRT glass can be used in the funnel glass and at least 15% in the panel glass. Higher recycling rates will be tested when enough suitable EOL CRT material is available. The logistic limitation for the reuse of separated EOL funnel glass will be around 55% of the melting capacity of the funnel tank. In practice in most cases a mixture of mixed glass and funnel glass will be used in the funnel tank to react on the distribution of fractions the market offers. In this case the highest recycling rate could be reached by using mixed glass as much as chemically possible together with separated funnel glass until the logistic limit would be reached for the sum of both fractions.

In laboratory scale testing promising results have been found in utilising lead-free part of the CRT colour panel glass in ceramic and glass production. With additives around 5% the reuse of EOL CRT in low temperature area (1000 °C) glazes and the production of construction blocks have been

successfully tested. In production of tableware glass, a test series with 100% of CRT glass with different production techniques (blowing, centrifugal and conventional casting) has been carried out. The results showed corresponding behaviour and properties to conventional glass material used in industry.

In order to be able to increase the recycling rates of CRT glass materials, the collection, packaging, processing and transportation systems of the EOL material have to be developed to ensure working safety and availability of high-quality raw material.

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# Part II

## Article II

**Raija Siikamäki, Leena Hupa**

# Utilisation of EOL CRT-Glass as a Glaze Raw Material





## Utilisation of EOL CRT –Glass as a Glaze Raw Material

Raija Siikamäki, Leena Hupa

**ABSTRACT.** In this study the use of recycled Cathode Ray Tube glass (CRT) as a raw material in tableware glazes is described. The recycling and industrial utilisation of CRT, a glass material from TV and computer sets, is a subject of intense research at the moment. The End-of-Life (EOL) CRT glass can be regarded as a very valuable silicate raw material, containing several metal oxides that impart beneficial properties in glasses and glazes. However, its use as a secondary raw material e.g. in the manufacture of TV glasses is restricted by the high demands of raw material consistency, which are not fulfilled by a foreign CRT cullet with a wide range of chemical composition.

Commercial glaze compositions typically contain natural raw materials with slightly varying chemical composition. Colour panel CRT glasses contain alkali and alkaline earth oxides at levels that roughly correspond to feldspars, a major raw material in many commercial glazes. Additionally, the CRT glass cullet contains barium, strontium and zirconium oxides, i.e. components that are often added to glazes because of their positive effect on glaze quality.

From this starting point a test series of glazes in which colour panel CRT glass is used as a substitute for feldspar was outlined. A commercial tableware glaze with high quality requirements was chosen as a reference glaze. The properties of the experimental glazes containing 4.5, 9.0 or 14.5 wt-% of the CRT glass cullet were tested and compared to the reference glaze. During glaze processing and firing, no significant differences to reference glaze could be detected. Further, the appearance of the glazes was fully comparable with the reference glaze. The long term chemical stability of the glaze was tested by a standard method. All the results indicate that CRT glass cullet is a potential glaze raw material in ceramic industry.

**Keywords:** Recycling of Cathode Ray Tube Glass, Properties of tableware glaze, End-of-life Cathode Ray Tubes

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## INTRODUCTION

During the past decades, the enormous growth of information technology and the increasing demands for recycling have put the manufacturers of Cathode Ray Tube (**CRT**) glasses in front of a challenging problem of finding new uses for the recycled End-Of-Life (**EOL**) glass cullet. The chemical composition of the glass used in different applications varies to such a degree that all the recycled glass originating from different manufacturers and different CRT applications cannot be used as a raw material in CRT manufacture.

The possibilities to recycle and industrially utilise the CRT glass cullet are actively researched. The widest research project on the subject so far has been Brite/Euram project RECYTUBE (BE96-3661) coordinated by Creed (Centre de Recherches et d'essais pour l'environnement et le Déchet, France). Department of Ceramics and Glass at the University of Art and Design has been one of the partners in the project. The research reported here was carried out within the RECYTUBE project.

Creed has forecasted that the total amount of EOL CRT glass in Europe should amount to 280 ktons in year 2003. [1] This glass material has different chemical compositions depending on the source, and can be divided into four main classes:

1. CRTs from Black & White (B&W) TV sets
2. CRTs from B&W PC monitors
3. CRTs from TV colour sets
4. CRTs from colour PC monitors

The chemical composition of different CRT materials varies a lot depending on the type of monitor. The compositions have changed as cathode ray tube technology has been developed. Further, each monitor is made out of two different glass parts of different chemical composition: the panel or the front part, and the funnel. Some typical chemical compositions of CRT glasses are given in Table 1.

Table 1. Some typical chemical compositions of CRT glasses according to SCHOTT [2]. The compositions are given in typical wt-% of each glass type.

OXIDE	COLOUR TV PANEL	COLOUR PC PANEL	COLOUR TV FUNNEL	PC FUNNEL
<b>Na<sub>2</sub>O</b>	8.0-8.6	6.6	6.3-6.8	5.45
<b>K<sub>2</sub>O</b>	7.0-7.5	7.3	7.8-9.7	8.05
<b>MgO</b>	0.2-1.3	0.33	1.0-1.8	1.5
<b>CaO</b>	0.5-2.5	1.15	1.4-3.8	3.5
<b>SrO</b>	1.5-8.5	8.65	0.15-0.5	0.5
<b>BaO</b>	10-12	1.15	1.0-1.95	3.5
<b>Al<sub>2</sub>O<sub>3</sub></b>	2.2-3.2	2.05	3.0-4.0	3.6
<b>ZrO<sub>2</sub></b>	0.2-1.5	0.95	0.08	0.1
<b>PbO</b>	0.0-0.1	0.05	14.7-22.7	20.25
<b>SiO<sub>2</sub></b>	60-62	59	52.0-59.0	53
<b>CeO<sub>2</sub></b>	0.25	-	-	-
<b>TiO<sub>2</sub></b>	0.4	0.6	0.05	0.07
<b>Sb<sub>2</sub>O<sub>3</sub></b>	0.25	0.5	0.05	-
<b>As<sub>2</sub>O<sub>3</sub></b>	0.02	0.02	0.01	-
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.07	0.12	0.06	-
<b>ZnO</b>	-	0.6	-	0.06

## **CLEANING OF THE RECYCLED CRT GLASS**

Beside the glass components a recycled CRT monitor contains also yoke and gun parts which have to be removed before further processing the glass into a secondary raw material. The glass phase components, the panel and funnel parts are sealed together but can be separated when processing the recycled EOL CRTs. Both the panel and the funnel are coated with layers containing several components, e.g. metal oxides, rare earth oxides and graphite. Also these components must be removed before recycling can take place.

In the RECYTUBE project, a method for cleaning and processing of the different recycled EOL CRT glasses into a secondary raw material to be used in diverse applications was suggested. Main steps in the multistage cleaning process are summarised below. In the first step, the monitors are sorted according to their origin into the four main classes given above. In the second step, the cathode ray tubes are dismantled, which starts with yoke and gun removal. After this, the panel and funnel units are separated and cleaned from the non-glassy components. The cleaning of the CRT glass can be done either by wet or dry cleaning methods, depending on the desired degree of material purity. The cleaned glass is powdered and screened, after which the material is ready to be used as a secondary raw material in different applications.

## **CRT- GLASS AS A GLAZE RAW MATERIAL**

The purified CRT glass cullet is a very valuable raw material, especially in applications where homogeneous silicate compositions are desired. Additionally, the CRT glass cullet contains barium, strontium and zirconium oxides, i.e. components that are often added to glazes because of their positive effect on glaze quality. Simplified, the cullet could be described as a homogeneous alkali-alkaline-earth -silicate containing some alumina but relatively much barium oxide. If starting from crystalline raw materials like sand and alkali carbonates, the formation and mixing of silicates to a homogenous material is a very energy consuming process. Thus, the homogeneous silicate glass cullet can be regarded as an energy effective raw material in applications where usually high temperatures are needed to ensure a desired product quality. A similar energy related aspect has been discussed when using feldspar in glass melting [3]. Further, the oxides introduced by the CRT-cullet are very important e.g. for imparting desired physical and chemical properties to glasses and glazes. The relatively high barium oxide content of the CRT-cullet does not restrict its use either in glass or glaze compositions. In these materials barium oxide is in fact frequently introduced to enhance some specific property.

The suitability of the cleaned EOL-CRT as a glaze raw material was tested by adding 4.5, 9.0 and 14.5 wt % of cleaned colour CRT panel glass in a commercial tableware glaze composition. The tableware glaze was chosen as a reference because of its high quality requirements, such as a desired colour, high chemical and mechanical stability as well as clearly specified viscosity requirements during the glaze firing stage. Also the compatibility of the glaze with the claybody is an important property usually expressed in the form of a specified thermal expansion.

The glass cullet tested contains alkali and alkaline earth oxides at levels that roughly correspond to feldspars, a major raw material in many commercial glazes. The easiest way to introduce the cullet to the glazes was to use it as a substitute for feldspar. It should be pointed out that feldspar typically is classified as a major raw material for introducing alumina to glass compositions, while in glazes its use is more or less justified because of its fluxing effect during firing. As the alumina content of

the CRT-cullet is considerably lower than in feldspars, the alumina balance was compensated for by clay minerals normally used to enhance the raw glaze properties.

The analysed chemical composition of the colour PC-panel glass cullet used in these experiments is given in Table 2. The table also shows compositions of two feldspars typically used in the reference glaze. The feldspar compositions are taken from the product specifications of the raw material supplier [4].

Table 2. Chemical compositions of the EOL CRT colour panel glass and two Finnish feldspars used in the experimental and reference glazes. The feldspars are commercial raw materials supplied by SP Minerals Oy Ab [4]. The compositions are given in wt-%.

Oxide	Finnish flotation Feldspar	Finnish Alavus Feldspar	Colour PC-panel Analysed *
SiO <sub>2</sub>	67.2	72.0	59.71
Al <sub>2</sub> O <sub>3</sub>	18.3	15.7	2.29
Na <sub>2</sub> O	5.0	3.7	8.26
K <sub>2</sub> O	7.7	7.5	7.73
MgO	>0.03	>0.03	1.13
CaO	0.5	0.2	2.84
ZnO	-	-	0.007
BaO	-	-	14.78
Fe <sub>2</sub> O <sub>3</sub>	0.13	0.03	0.093
Density	2.59 g/cm <sup>3</sup>	2.61 g/cm <sup>3</sup>	2.72 g/cm <sup>3</sup>

\* + BaO 7-5, PbO <0.1, Sb<sub>2</sub>O<sub>3</sub> <0.5, ZnO <0.5, Zr O<sub>2</sub> 0-3

### Calculating the glaze compositions

In the manufacture of the commercial reference glaze the suitability of the reference glaze for the claybody is typically characterised as mole fractions of silica to alumina and of lime to magnesia, as given in Table 3. The substitution of feldspar with the CRT cullet was done by adjusting the glaze compositions according to these production-specific mole fraction numbers.

In order to maintain the firing properties as well as the final properties of the glaze unchanged the total raw material and final oxide composition of the glaze have to be adjusted in a controlled manner to allow the addition of the new raw material, CRT cullet. Several properties of homogenous glazes can be calculated with adequate accuracy additively from its chemical composition by using models given in literature. The firing behaviour of a homogeneous glaze can be described by its viscosity-temperature behaviour. The glaze compatibility with the base is easily checked by thermal expansion. In this work, viscosity models by Lakatos [5] and expansion models by Appen [6] were used to check that the calculated properties of the experimental glazes vary within an acceptable range compared to the reference glaze. The calculated values of these properties of all the experimental glazes are given in Table 3. The table also lists the calculated properties for the glass cullet. The small variations in the property values of the CRT-containing glazes compared to those of the reference are within an acceptable level, and thus do indicate no deterioration in the firing behaviour or final glaze properties.

All the calculated compositions were tested in practice to ensure the actual glaze behaviour.

Table 3. Calculated property values for the reference and experimental glazes, and for the CRT glass cullet used in the experiments.

Oxide	Ref. mole-%	A mole-%	B mole-%	C mole-%	CRT mole-%
<b>Mole fraction</b>					
Si / Al	8.00	7.91	7.95	7.98	44.30
Ca / Mg	7.02	7.10	7.07	7.08	0.27
<b>Thermal exp. (K<sup>-1</sup>)</b>					
$\alpha / 10^{-7}$	52.91	54.41	54.03	53.44	107.5
<b>log viscosity (dPas)</b>	<b>Temp. (°C)</b>	<b>Temp. (°C)</b>	<b>Temp. (°C)</b>	<b>Temp. (°C)</b>	<b>Temp. (°C)</b>
5.84	1000	993	995	998	788
5.29	1050	1042	1044	1047	833
4.82	1100	1090	1093	1096	878
4.41	1150	1138	1142	1146	923
4.04	1200	1188	1192	1196	969
3.72	1250	1237	1241	1246	1014
3.44	1300	1284	1289	1294	1058

**Glaze A:** addition of 14,5 wt-% of CRT cullet, **Glaze B:** addition of 9,0 wt-% of CRT cullet

**Glaze C:** addition of 4,5 wt-% of CRT cullet

## PREPARATION OF THE GLAZED PRODUCTS

### Non-decorated tableware

The test samples were prepared according to the normal processing of the reference commercial glaze. Batches weighing 10 kilograms were mixed in water and ball-milled. After milling the glazes were magnetic-sieved. The particle size distribution was analysed and weight/litre ratio of the glaze was adapted to the density of spray glaze.

The ceramic body used in the test series was dry-pressed stoneware. Each experimental glaze was sprayed on about 20 products, including plates and bowls. Different forms were used to be able to observe the glaze behaviour in the glazing process. The glazed products were fired at 1260 °C in the gas-fired furnace used in the production of the reference ceramic.

All the products, glazed with the CRT glass cullet containing glazes or the reference glaze, were fired in the same firing in order to avoid potential changes in the impact of the furnace atmosphere.

### Decorated tableware

A set of samples glazed with the experimental glazes containing the CRT cullet was decorated with silk screen transfers. The decorations were fixed on the glazed ceramic body in a separate firing

step. This additional firing step requires that the glaze should be suitable for firing twice without failing in final quality. Also, the glaze should be compatible with the decorations used. The transfers used in the test set contained a variety of twenty different pigments. The decoration firing was done to the temperature of 1150 °C with the total firing time 5 hours.

## TESTING OF THE GLAZE PROPERTIES

### Raw glaze

The raw glaze properties refer to the behaviour and properties of the glaze before firing, both in the glaze suspension and in the dry glaze coating on the ceramic before firing. The behaviour of experimental glazes was similar to the reference glaze in all the stages of the raw glaze processing. The particle size distribution with 3 different milling times was checked and compared to the reference glaze. The similar particle size distribution was found with the same ball milling time as in the reference glaze.

Green strength of the glaze refers to how well the glaze is fixed on the clay-body before firing. The clay minerals in the glaze suspension are typically important for the green strength. The influence of the glass cullet on the glaze composition was compensated for rather by increasing than decreasing the amount of the clay minerals. This means that the green strength, as observed in practical processing, was at least as good as that of the reference glaze.

### Firing behaviour

The firing behaviour described by calculated viscosity values of the molten homogenous glaze give a rough guess of the firing behaviour at high temperatures. However, the reactions in the glaze and in the clay-body during the heating period to the final firing temperature are very important for the final glaze quality. This means that in designing glaze compositions a desired sintering of the clay-body has also to be taken into account. The main weight loss during firing of both the glaze and the body arises from the escape of the chemically bound water in clays. This water loss typically takes place at temperatures higher than 400 °C. The feldspar in the reference glaze melts at temperatures above 1000 °C. Replacing some or all of feldspar by a homogeneous glass, which softens at a lower temperature than 1000 °C, might cause some faults in the final glaze quality. In all, the reactions and their kinetics at the body-glaze interface are complex and difficult to measure. The reactions taking place in the solid state in the raw materials as given by thermal analysis offer one possibility to estimate the early firing behaviour. However, the glaze quality in terms of properties, glaze faults and glaze appearance after firing gives the final evaluation of the compatibility of the glaze with the clay-body used.

The reactions during the initial firing stage, i.e. within the temperature range for the water drive-off from the clay, were studied by thermal analysis. Differences in the onset of the reactions or their extent in terms of weight change might indicate some problems with the compatibility of the test glazes with the clay-body. The weight loss curve and the TG-curve for the glaze with the highest content of the CRT-cullet and for the reference glaze are given in Figure 1 and Figure 2. The weight loss curve shows the temperature ranges for the burn-off of water and organic materials. The peaks on the TG-curve show physical or chemical changes taking place in the mixture around the indicated temperatures. The curves are in this context used only to a simple comparison of the trends in the two glazes during heating period. As the figure shows, the main reaction in both glazes commences at roughly 600 °C and declines at 720 °C. Thus, the replacement of feldspar in the glaze composition seems not to affect the solid state reactions in the glaze.

The inspection of the fired products reveals that the glaze surface after the firing is glossy and well molten in all the test glazes. Thus, the replacement of feldspar with the CRT cullet gives glazes with apparent firing behaviour fully comparable to the reference glaze.

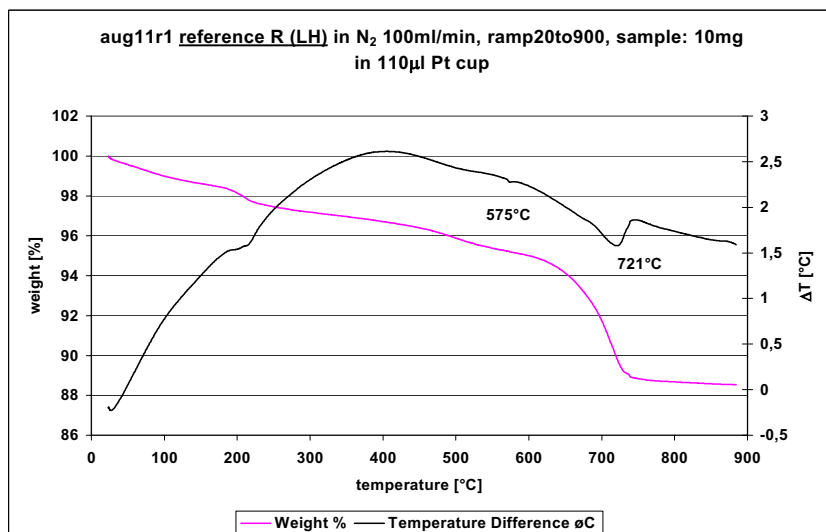
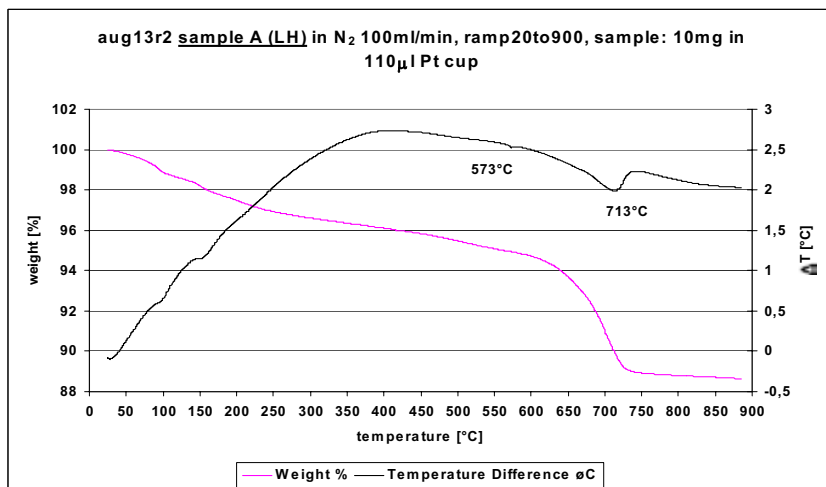


Figure 1 and 2. Weight loss (*Weight*[%]) and TG (*ΔT*[°C]) curves for the glaze containing 14,5 wt-% of CRT cullet. Sample size 10 mg, heating rate 10 °C/min.

## Measurements of the glaze colour

Glazes for the tableware products should contain no heavy metals that could cause miscolouring. As shown in the Table 2, the content of  $\text{Fe}_2\text{O}_3$ , a common impurity, is of the same level in the purified CRT-glass cullet and in the feldspars used. The glaze colour should thus not suffer from the substitution of feldspar with the cullet. The colour measurements made with a Dr. Lange GmbH (Spektromess Oy) spectrophotometer confirm the assumptions made on the chemical composition of the raw materials.

The colour was measured by using the light source D65 using the standard three-point system. The glaze thickness varies slightly mainly because of the shape of the product. In order to get a consistent and representative result of the colour hue, each sample was measured at three different areas. The measured values were expressed according to different standard colour measuring systems used in glaze industry. The colour values given in Table 4 are the average of these measurements with different colour systems. As can be deduced from the small differences between the given values for each colour measuring method, the colour of the CRT cullet containing glazes is fully comparable with the commercial reference one.

Table 4. Averaged colour values of the experimental and reference glazes as given by the standardised systems according to CIE-Lab (L: brightness, complementary colour axis; a: red-green [+a: red, -a: green] and b; yellow-blue [+b: yellow, -b: blue]) X,Y,Z –values, Chromacity and Hunter-Lab.

	REF.	GLAZE A	GLAZE B	GLAZE C
<b>L*</b>	85.49	88.24	87.14	85.38
<b>a*</b>	-0.61	-057	-0.66	-0.52
<b>b*</b>	5.83	6.13	6.42	6.31
<b>X</b>	63.23	68.54	66.39	63.07
<b>Y</b>	66.97	72.57	70.33	66.77
<b>Z</b>	64.93	70.19	67.61	64.18
<b>X</b>	0.3240	0.32344	0.3249	0.3251
<b>y</b>	0.3432	0.3434	0.3442	0.3441
<b>Y</b>	66.97	72.57	70.33	66.77
<b>L</b>	81.83	85.19	83.84	81.71
<b>a</b>	-0.59	-0.56	-0.64	-0,50
<b>b</b>	5.30	5.65	5.87	5.72

## Washing tests of undecorated tableware

The surface quality of the glazed products was checked before the washing with an optical microscope with a magnification of 40 times. The glazed products were washed in a dishwasher with the same procedure as is used for the quality control of the reference glaze. The washing procedure and chemicals are shown in Table 5. The optical surface quality control of the glazed products was repeated after 250, 500 and 1000 washings.



Table 5. The used machinery and chemicals for the washing tests

Dishwasher	Metos Master 515/ 3 minutes washing program
Detergent	QED/ Diversey Oy / dosage 1,5 g/litre
Scavenging agent	Divo 80 / Diversey Oy

The deterioration of the glaze surface is usually checked further with a so-called knife test, in which the surface is scarped with a knife. If the glaze surface is of poor quality or if the surface has deteriorated during the washing cycles, a scratched surface with typical dark lines showing tracks of the knife will be observed.

The experimental glazes before the washing tests showed less non-molten quartz than the reference one. This observation is likely to depend on the substitution of the feldspar with the CRT cullet. The feldspar used consists mainly of the minerals orthoclase and albite, and a few per cent of free quartz. The free quartz in the glaze is thus eliminated in the glaze by the glass cullet.

The presence of non-molten quartz on the glaze surface is one of the main reasons for the metal of cutlery to cause dark scratches to the glaze surface. The dark scratches in the surface of the experimental glazes were less pronounced than in the reference glaze. The experimental glazes had also otherwise maintained well their shiny surface without any failures.

### Washing tests of decorated tableware

The washing tests of the decorated ware were similar to the non-decorated ones. The results showed that the transfers, moved with a layer of lacquer to the surface of the objects, were more susceptible to dark scratches from cutlery. Especially on the light colour pigments, e.g. yellow tones, marks could be observed often. However, a similar phenomenon occurred to some extent with the objects glazed with reference glaze.

### Leaching of heavy metals from the surface

The typical chemical compositions in Table 1. show that the CRT glasses contain heavy metal oxides such as lead oxide and barium oxide. The leaching of especially lead from the glazes has in practice lead to total elimination of lead from tableware ceramics. Also the leaching of barium from the glazes has evoked growing concern in the ceramic industry. The leaching test of heavy metals is usually carried out according to the standard method ISO 7086. The maximum acceptable amounts of the oxides of lead and chromium leached from tableware glasses in the standardised method are given in Table 6. So far, no limits have been set on the leaching of barium oxide from glazed ceramic cookware. Table 6. also shows the leaching results from the experimental glaze containing the highest amount of CRT- glass cullet. In this test, also the leaching of barium was measured. It should be pointed out that barium content in the CRT colour panel glass is relatively high. The addition of 14.5 wt-% cullet gives 2.14 wt-% of BaO in the glaze.

Table 6. Limits of maximum allowed leaching of heavy metals from ceramic cookware and leaching test results of the experimental glaze containing 14.5 wt-% CRT-cullet. All the values refer to a method performed according to standard ISO 7086.

	Limit (volume <1.1 litre)	test sample A
Pb:	< 5.0 ppm	<0.010 ppm
Cd:	< 0.5 ppm	<0.001 ppm
Ba:	-	<0.50 ppm

According to the leaching test, the content of the heavy metals in the test liquid is well below the maximum allowed limits. The leaching of the barium, less than 0,50 ppm, seems to be minor compared to its original content in the glaze. As long as the regulations for acceptable barium contents are missing, this test result cannot be further classified. However, it is advisable to measure the leached barium levels, at least when the glaze composition is adjusted substantially.

## CONCLUSIONS

The secondary raw material originating from the recycling and purification of end-of-life cathode ray tube glasses is a valuable raw material, which can be used in glaze manufacture. Glaze manufacture is a complicated industrial process, where several aspects of the raw materials used should be taken into consideration.

The raw glaze properties of the compositions containing the glass cullet raw material were very similar to the reference glaze containing feldspars.

No marked differences in the firing behaviour of the experimental glazes and the reference glaze could be observed. However, the experimental glass cullet containing glazes contained after firing a lower content of non-molten raw quartz. The occurrence of quartz in the glaze surface gives rise to a lower hardness of the glaze. The quartz containing areas are easier scratched in a knife test. Repeated washing cycles are likely to deteriorate the glaze surface in these free-quartz rich areas. Thus, the elimination of free quartz from the glazes by introducing a homogeneous material, glass cullet, is likely to improve the mechanical and long-term stability of the glaze.

The content of colouring agents in the glass cullet from the cathode ray tubes is of such a level that they should not impart any colour hues in the glaze. However, the content of heavy metals, especially barium oxide is relatively high and the possible leaching of the barium should always be tested. So far, there are no regulations of maximum allowed leaching of barium from tableware ceramics. The tests indicate that the amount of barium leached from a tableware glaze containing 2.14 % barium oxide is very low.

The results indicate that glass cullet from the end-of-life cathode ray tubes can be used as a raw material in glazes for tableware ceramics, which are products strictly controlled by legislation and by consumers. Since the recycled material shows applicable behaviour in such a demanding application as tableware glaze, its use in some other ceramic application would also be possible. Larger quantities of recycled CRT glass could be used to building ceramics, e.g. to tile glaze.

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# Part II

## Article III

**Raija Siikamäki**

# End-of-Life Cathode Ray Tube Glass as a Raw Material for Hollow Ware Glass Products



# **End-of-Life Cathode Ray Tube Glass as a Raw Material for Hollow Ware Glass Products**

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**ABSTRACT** The recent Decision of the European Communities 200/532/EC classifies discarded electrical and electronic equipment containing hazardous components, such as glass from cathode ray tubes, as hazardous waste which cannot be landfilled. Further, according to the WEEE directive (Waste Electrical and Electronic Equipment) the reuse and recycling of material and substance has to be at least 65 % by an average weight per appliance. In TV sets and display terminals the glass comprises roughly 65-70 % of the total mass. Thus, in the reuse of End-Of-Life (EOL) Cathode Ray Tubes (CRT) the industry is facing new challenges. Recycled EOL Cathode Ray Tube glass can on one hand be regarded as a valuable silicate material but on the other hand it is a problematic material requiring a multistage treatment consisting of separation, cleaning and crushing for achieving an acceptable compositional range. One obstacle for the reuse is wide range of different chemical compositions used in Cathode Ray Tube glasses.

In this study the use of CRT glass as a raw material for hollow ware glass products has been tested. Three different fractions of CRT panel glass (PC, TV and mix of those) were melted in a laboratory furnace for evaluating their melting properties. The working properties by using different glass forming techniques, like blowing and casting (centrifugal and conventional casting) were characterized in an industrial production furnace. The first test series was carried out with recycled material collected from Central Europe and the later ones with material collected from Finland. The results indicate that by adjusting the melting time and - temperature suitably the melting and working properties typical for conventional glasses can be maintained also when using up to 100 wt % recycled CRT glass as a raw material. Products in tableware use having contact with food must have an excellent chemical durability. The durability was measured with a standard leaching test. The high durability of the glasses indicates that the recycled CRT glass cullet is a feasible raw material also in industrial manufacture of blown or casted glass products.

**Keywords:** Recycling of Cathode Ray Tube Glass, End-of-life Cathode Ray Tubes, Hollow ware glass production, tableware glass products, melting of cullet

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## INTRODUCTION

The waste stream of electrical and electronic equipment has been identified as one of the fastest growing waste streams in the European Union. Today this waste stream constitutes of 4% of the municipal waste, and is assumed to increase by 16-28% every five years. This represents a growth three times faster than the average municipal waste [1]. In order to reduce the amount of electrical and electronic waste disposed of in landfills and incinerators, the waste classification and the WEEE directive seek to establish separate collection and recycling systems for electrical and electronic waste. WEEE directive also implements the principle for producers to take into account, already at the product design stage, the need to reduce the use of hazardous substances and to improve the recyclability of electrical products. These decisions will increase challenges to find out possible reuses for End-of-Life Cathode Ray Tube glass.

Many different application areas for the reuse of CRT glass are needed in order to be able to achieve the recycling target set. In application areas like in glass industry, a closed loop recycling is an important way to reuse the recycled CRT glass, but also open loop applications are possible in glass industry. In developing closed-loop recycling, some CRT producers have made remarkable progress: at the moment more than 35% of EOL CRT glass can be used in the funnel glass and at least 15% in the panel glass. Higher recycling rates are being tested at the moment, but closed loop recycling cannot still utilise all the material coming from market.

In hollow ware glass production recycled glass has become an increasingly important raw material, which has helped to reduce the energy consumption and to shorten production times in glass industry, especially in the manufacture of container glass. Container glass industry receives enough recycled material from the collection of packing waste. The cost of this recycled glass is quite low in comparison to CRT glass which requires a cleaning process before any recycling can take place. Also the chemical composition of CRT glass set special limits for the utilisation in package glass industry: the composition and the properties it brings along differ greatly from the glass composition used for container glass.

In tableware production the main source of cullet has been internal rejects. Usually the recycled cullet is clear glass. The coloured glass is mostly used as a thin layer with layers of clear glass surrounding it and that makes rejects difficult to reuse. Glass material with even colour enables well the recycling process. An additional advantage of using cullet is the lower energy consumption due to lower melting temperature of cullet when compared to use of batch.

The sector of tableware glass production consists mostly of small and medium size enterprises, but the total production in the EU is considerable. The yearly production of tableware glass is approximately 900 000 tonnes. The EU is the world's largest exporter of glass tableware [1], [2].

## EXPERIMENTAL MATERIALS

In open loop applications it is required that the CRT glass cullet is lead-free. The main parts in CRT are the panel (front part) and the funnel. The lead content in funnel is 11-24 PbO wt%, and the sealing frit connecting the two main parts contains up to 85 wt% PbO. In black and white monitors also the panel glass might contain some lead. Thus, only the lead-free panel from colour devices is a possible raw material for open loop applications. The recycling of the CRT glasses requires a careful separation process, in which the black and white monitors as well as the funnel and neck



parts of the colour monitors are sorted out from the lead-free panel glass. In the cleaning step the coating should also be separated from the glass.

The chemical composition of purified CRT colour panel glasses and conventional tableware glasses are given in Table 1. The table also shows calculated values of several physical properties of the glasses.

Table 1. Analysed chemical compositions of EOL CRT colour panel glasses and a commercial tableware glass. The EOL CRT glasses were collected in Finland during 2001-2002. The viscosity values are based on the model by Lakatos [4], and the other properties on the models by Appen [5].

	CRT panel glasses wt%			Commercial tableware glass wt%
Oxide	Colour PC	colour TV	mix	
SiO <sub>2</sub>	60.3	61.6	61.4	69.0
Al <sub>2</sub> O <sub>3</sub>	2.37	3.26	3.17	0.37
Na <sub>2</sub> O	8.36	8.57	8.45	10.2
K <sub>2</sub> O	7.55	7.36	7.11	7.4
Li <sub>2</sub> O	-	-	-	0.19
MgO	0.19	1.05	0.99	0.035
CaO	0.96	2.30	2.14	3.6
ZnO	0.23	0.08	0.12	2.26
BaO	8.87	10.52	10.51	5.3
B <sub>2</sub> O <sub>3</sub>	-	-	-	1.23
Fe <sub>2</sub> O <sub>3</sub>	0.22	0.058	0.058	0.029
SrO	9.25	3.81	4.28	-
Sb <sub>2</sub> O <sub>5</sub>	0.44	0.57	0.62	-
As <sub>2</sub> O <sub>5</sub>	0.03	0.11	0.08	-
PbO	0.011	0.32	0.060	-
T/°C	log (η/dPas)			
500	12.89	13.40	13.44	13.24
600	9.59	9.81	9.85	9.53
700	7.51	7.60	7.64	7.31
800	6.09	6.10	6.14	5.83
900	5.05	5.02	5.05	4.77
1000	4.25	4.20	4.23	3.98
1100	3.36	3.56	3.59	3.36
1200	3.13	3.05	3.07	2.87
1300	2.71	2.62	2.65	2.47
1400	2.36	2.27	2.29	2.13
1500	2.07	1.97	1.99	1.85
exp.1/K	10.07-06	10.20-06	10.07-06	99.70-07
Density g/cm <sup>3</sup>	2.5733	2.6269	2.6191	2.555
refr. index	1.5155	1.5233	1.5222	1.520

## **PROCECCING OF EXPERIMENTAL GLASSES**

The glasses used in the experiments were collected from Western Finland during years 2001-2002. While dismantling the apparatus with hot wire technique, the different glass parts of CRT's were separated into five different categories:

- 1) colour pc-panel glass
- 2) colour tv-panel glass
- 3) mix colour panel (tv & pc)
- 4) funnel glass
- 5) mixed glass (containing e.g. black&white CRT)

The three first categories were used as experimental material in this study. After dismantling the coatings were vacuum cleaned from the panel glass with cullet size of 1 – 200 mm. The glass was crushed and sieved into three different particle fractions: below 1 mm, 1-3 mm and over 3 mm. Particle size fraction over 3 mm. was used as a test material in this study.

## **MELTING TEST OF CRT GLASSES IN LABORATORY FURNACE**

The melting parameters for the three categories of the CRT panel glass (PC, TV and mix of those) were studied by melting the glasses in an electrically heated laboratory furnace. The batches of 300 g were melted in high-alumina crucibles. The temperature in the furnace is measured by a Pt/13% Rh-Pt thermocouple system with an accuracy of  $\pm 2$  C°.

The meltings were carried out at different temperatures for 3 to 4 hours and batch additions of 10% and 20%. The chemical composition of batch used is shown in the Table 1. (commercial tableware glass). The glass was charged twice into the crucible; the first half when the furnace reached the melting temperature and the other half after half an hour from first charging. The molten glass samples were cast in a graphite mould and annealed overnight.

The images of the glasses in Figure 2 show the number and size of the bubbles evolved in the glasses melted at different temperatures and for different times. The figure also shows the behaviour of the reference tableware glasses at the same melting conditions.

The number and size distribution of the bubbles and seeds in the glasses are given in Table 2 and in fotos taken throught an optical microscope in Figure 1. The CRT cullet based glasses clearly contain a greater number of small seeds than the commercial tableware glass, when melting time is short. Total amount of bubbles and seeds in a glass sample melted for 4 hours at 1400 °C is higher in CRT glass than in the commercial tableware glass. The longer melting, even in temperature 100 °C lower, gives the best result of refining. Batch addition of 10% gives better result in comparison to addition of 20%. Comparing the samples with batch addition to cullet-based meltings, the result indicates that the melting without any additives is possible.

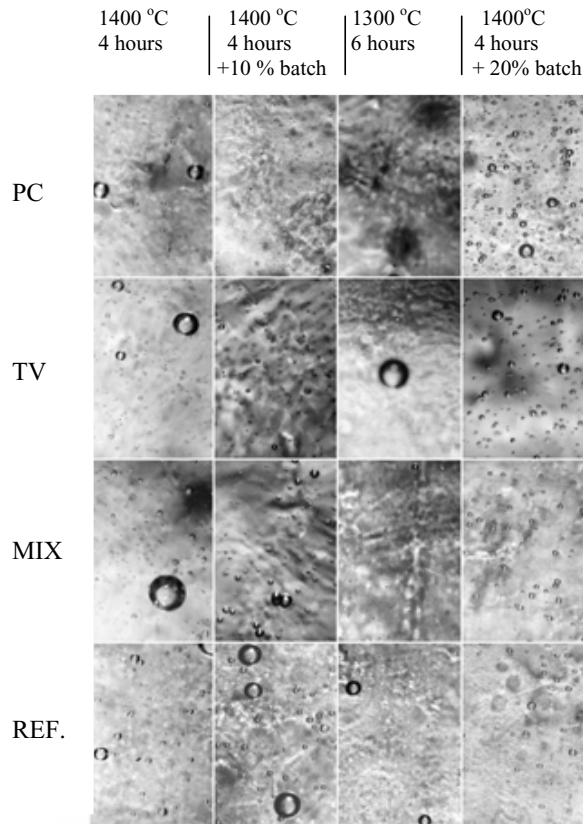


Figure 1. Images showing the number and size of the gaseous inclusions left in the glasses melted according to different melting and charging parameters.

Table 2. The number and size distribution of the bubbles and seeds in the glasses (series I with batch addition of 10%, series II cullet based melt and series III with batch addition of 20%).

Sample (melting temperature/- time)	total	<1mm	1mm - 5mm	>5mm
PC (1400°C/ 4 h)	141	122	17	2
TV (1400°C/ 4 h)	175	148	23	4
MIX (1400°C/ 4 h)	198	145	51	2
REF. (1400°C/ 4 h)	74	16	54	4
PC-I (1400°C/ 4 h)	33	20	13	-
TV-I (1400°C/ 4 h)	144	97	47	-
MIX-I (1400°C/ 4 h)	122	61	56	5
REF.-I (1400°C/ 4 h)	81	18	58	5

Sample (melting temperature/- time)	total	<1mm	1mm - 5mm	>5mm
PC-II (1300°C/ 6 h)	15	13	1	1
TV-II (1300°C/ 6 h)	3	2	-	1
MIX-II (1300°C/ 6 h)	36	26	10	-
REF-II (1300°C/ 6 h)	66	58	6	2
PC-III (1400°C/ 4 h)	484	420	60	3
TV-III (1400°C/ 4 h)	194	72	117	5
MIX-III (1400°C/ 4 h)	66	11	55	-
REF-III (1400°C/ 4 h)	67	21	45	1

## MELTING IN INDUSTRIAL FURNACE

The melting experiments in the laboratory furnace show the difference in the melting behaviour between the different glasses. However, the melting parameters suggested by laboratory tests cannot directly be applied to industrial furnaces. The melting properties as well as the working properties were further tested by melting the glasses in an industrial 150 kg pot furnace fired with natural gas. The temperature was measured by a stationary thermometer and the verification of the temperature associated with each operation was done with a portable optical thermometer.

Table 3 . Melting schedule for CRT colour panel -cullet

time	Operation	temperature
	first charging (75 kg)	1240 °C
2.00	second charging (75 kg)	1240 °C
5.00	first mixing of a melt	1240 °C
5.30	second mixing of a melt	1240 °C
14.00	a ready melt	1240 °C
15.00	furnace in a working temperature	1190 °C

## FORMING: centrifugal casting

Furnace temperature while casting was 1095 °C. Molten glass was cast to iron moulds and the rotation was started. Rotation speed of the centrifuge was 500 turns/minute and time for the piece to be ready was 4-6 seconds. After forming the products were annealed. The mould needed 8-12 seconds cooling time with compressed air between the castings.

The CRT-glass material was found to be a suitable material for centrifugal casting process. The thermal behaviour in production process is comparable to the glass material the plant is using in tableware production. Moreover, the annealing schedule does not differ considerably from the annealing cycle used in normal production.

### **FORMING: casting**

Furnace temperature while casting was 1190 °C. Molten glass was casted to graphite and iron molds. The formed pieces were annealed according to the thickness of the product to room temperature. The thermal behaviour of CRT panel glass is well suited for casting process; the glass was cooling evenly and faster than reference material.

### **FORMING: blowing**

Furnace temperature while blowing was 1195 °C. Blowing was proceeded as mould blowing to a wooden mould and as free blowing. The difference to the glass material the plant is using can be noticed especially in free blowing, when the piece is not formed in the mould but with hand tools. The working range of CRT-glass is shorter. Otherwise thermal behaviour in blowing process is comparable. Mould and free blown pieces in most cases do need a cold working process, grinding and polishing, too. The test pieces have gone through the normal process without any failure.



Figure 2. Products made from EOL colour panel glass with different production techniques. On the right blown cylinder (ø 100 mm, height 220 mm), centrifugal casted bowl (ø 160 mm) and casted candleholder (ø 115 mm) and in the picture on the left to a iron mold casted platters (ø 250 mm and ø 360 mm).

### **CHEMICAL DURABILITY OF TEST PRODUCTS**

The products were tested with a procedure applied for testing the reference tableware products. The samples were examined before the washing; the surface quality was checked with an optical microscope with a magnification of 40 times. These controls were repeated after 250, 500 and 1000 washings. The washing procedure and chemicals are shown in Table 4. The appearance of tableware products manufactured of the CRT glasses did not differ from the reference pieces after the washing tests.

Table 4. The machinery and chemicals used in the washing tests

The dishwasher:	Metos Master 515/ 3 minutes washing program
The detergent:	QED/ Diversey Oy / dosage 1,5 g/litre
The scavenging agent:	Divo 80 / Diversey Oy

Tableware products used in contact with food must have an excellent chemical durability. Leaching tests were performed with a standard method (DIN 12111). The leaching tests gave no difference in chemical durability between the reference commercial tableware glass and the experimental glasses made of recycled CRT glass cullet. Further, no release of elements classified as toxic (BaO, ZrO, As<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>) was detected from the experimental glasses.

## CONCLUSIONS

Industrial melting tests have been performed with 100% recycled CRT colour PC panel glass by using different production techniques: blowing, casting and centrifugal casting. The overall melting properties of the experimental glasses were acceptable. One observed difference to the commercial tableware glass used as the reference was some cords in some experimental glasses. The working properties of the glasses were satisfactory. According to the experiments performed, recycled CRT cullet can be formed with various methods applied in tableware glass industry.

The tableware products made from glasses melted industrial furnace were tested for the chemical durability by washing tests (500 and 1000 washing) without any failure. Also the leaching tests performed according to a standard method indicate that recycled CRT glass can be used as a raw material for manufacturing tableware products.

## ACKNOWLEDGEMENTS

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# Part II

## Article IV



**Raija Siikamäki**

Glaze for Low-Fired Ceramics  
from End-of-Life  
Cathode Ray Tube Glass



## **Glaze for Low-fired Ceramics from End-of-life Cathode Ray Tube Glass**

**ABSTRACT.** This study discusses the use of Cathode-Ray-Tube (CRT) panel glass, i.e. the lead-free part of CRTs, as a raw material for glazes to low-fired ceramics. Three different fractions of CRT glasses - colour-TV panel glass, colour PC panel glass and a mixture of colour TV and PC panels, were tested in order to find the best glass material for this application area. For background information, the thermal behaviour of these experimental materials in the temperature range 40-1200 °C was measured by heating microscope. The test glazes contained 86-96% of cleaned and crushed CRT glass. Physical properties such as thermal expansion were adjusted by adding ceramic raw materials typical for conventional glazes. Three different earthenware compositions were used as clay body for test samples. Commercial glaze for low-firing temperature was used as a reference. The clear, colourless, base glaze mixture was also coloured with ceramic pigments in order to determine its suitability to function as a base glaze for coloured glazes. The gloss of the fired test samples was measured. Also the chemical durability in an alkaline solution was tested. The different measurements as well as the visual appearance of experimental glazes indicate that CRT glasses are potential raw materials for glazes used on ceramics fired to low temperatures.

**Keywords:** Recycled Cathode Ray Tubes, End-of-Life Cathode Ray Tubes, Glaze raw materials, Low fired glazes, Glaze for earthenware

**LA R Siikamäki** is a researcher in the School of Design, Ceramics and Glass, at the University of Art and Design Helsinki. There she has also worked as a part-time teacher for eleven years. Her teaching area has been glass material studies. Her research interest is the utilisation of recycled materials in ceramic and glass industry.

## INTRODUCTION

The use of EOL CRT glasses as a one of the raw materials for glazes to high firing temperatures (1260 and 1350 °C) has been tested during RECYTUBE (Integrated Recycling of End-of-Life Cathode Ray Tube Glass) project [1],[2]. Experimental glazes contained 4.5-35 weight-% EOL CRT glasses. In this application area glass cullet can be regarded as an energy efficient, homogenous silicate raw material. In this study, the suitability of the cleaned EOL CRT glasses as a raw material for low firing range of ceramics was tested.

For the glazes fired in a low temperature, fluxes are an essential part of the compositions. Lead compounds are used often as a flux since lead imparts brilliance and lead glazes are tolerant to varying firing parameters. However, lead glazes always have the disadvantages of potential health hazards both during the manufacturing process and in finished products. The purified colour panel glasses could be introduced to glazes for low firing temperature area as a lead free frit. The valuable properties of CRT glasses can be utilized to the full and can give high value recycling to the CRT glasses.

## PROCESSING OF EXPERIMENTAL GLASSES

The glasses used in the experiments were collected from Western Finland during years 2001-2002. While dismantling the apparatus with hot wire technique, the different glass parts of CRT's were separated into five different categories:

- 1) colour PC panel glass
- 2) colour TV panel glass
- 3) mix colour panel (TV & PC)
- 4) funnel glass
- 5) mixed glass (containing e.g. black & white CRT's)

The three first categories were used as experimental materials in this study. After dismantling the coatings were vacuum cleaned from the panel glass. The cleaned glass was crushed and sieved into three different particle fractions: below 1 mm, 1-3 mm and over 3 mm. Particle size fraction below 1 mm. was used as experimental glaze material in this study.

## EXPERIMENTAL MATERIALS

The chemical compositions of purified CRT glasses used in this study, cf. Table 1., were analysed in order to evaluate the efficiency of the cleaning process and to measure the differences in their compositions. The content of lead oxide in glasses is between 0.011-0.32, i.e. a level that does not exceed typical lead oxide impurity contents in some raw materials for glasses. This indicates that the degree of the cleaning of the test glasses is very good: the separation of lead-containing parts, funnel and sealing frits, has thus been successful.

The differences in the chemical compositions of three different glassy materials, TV, PC and mixture of TV and PC colour panels (later in the text: mix), are relatively small for

all other oxides but strontium oxide. In the experimental materials its content varies between 3.81 in the colour TV panels and 9.25 weight-% in the PC colour panel glass.

Table 1. Analysed chemical compositions of the experimental EOL colour panel CRT glasses in weight-%

Oxide	PC	TV	MIX	Uncertainty (C.L. 95 % i.e. 2s)
SiO <sub>2</sub>	60.3	61.6	61.4	± 0.4
Al <sub>2</sub> O <sub>3</sub>	2.37	3.26	3.17	± 0.10 – 0.15
Fe <sub>2</sub> O <sub>3</sub>	0.22	0.058	0.058	± 0.002 – 0.007
CaO	0.96	2.30	2.14	± 0.02 – 0.04
MgO	0.19	1.05	0.99	± 0.004 – 0.02
PbO	0.011	0.32	0.060	± 0.001
Na <sub>2</sub> O	8.36	8.57	8.45	± 0.14
K <sub>2</sub> O	7.55	7.36	7.11	± 0.11
TiO <sub>2</sub>	0.39	0.32	0.33	
BaO	8.87	10.52	10.51	
SrO	9.25	3.81	4.28	
ZnO	0.23	0.08	0.12	
As <sub>2</sub> O <sub>5</sub>	0.03	0.11	0.08	
Sb <sub>2</sub> O <sub>5</sub>	0.44	0.57	0.62	

## SINTERING PROPERTIES OF THE EXPERIMENTAL GLASSES

The sintering properties of the experimental glasses were measured by a heating microscope (Misura 3.0., Expert Systems) in the temperature range 500-1200 °C. The heating rate was 5 °C/min, and the sample was imaged at every 5 °C. The height of the sample was measured from these images. The temperatures typical side view shapes and during sintering, i.e. the first shrinkage of the sample indicating the commencement of the sintering, the half sphere indicating that the viscosity is around 10<sup>4,5</sup> dPas and finally a third-sphere describing the floating out of the sample are given in Table 2.

Table 2. Temperatures for the characteristic side views describing the proceeding of sintering of the experimental glasses during constant heating in a heating microscope.

sintering temperature	MIX 605 °C	PC 625 °C	TV 640 °C
½ sphere	TV 835 °C	PC 870 °C	MIX 875 °C
melting temp.	TV 920 °C	PC 950 °C	MIX 970 °C

The sintering curve shows slight differences in the sintering behaviour of the experimental glasses. When comparing the characteristic sample forms during heating the mix glass shows the lowest sintering temperature and highest temperature for TV glass. TV panel glass demands the highest sintering temperature, thus when temperature is raising the viscosity of the glass changes more rapidly compared to the PC and mix glasses (Figure 1.).

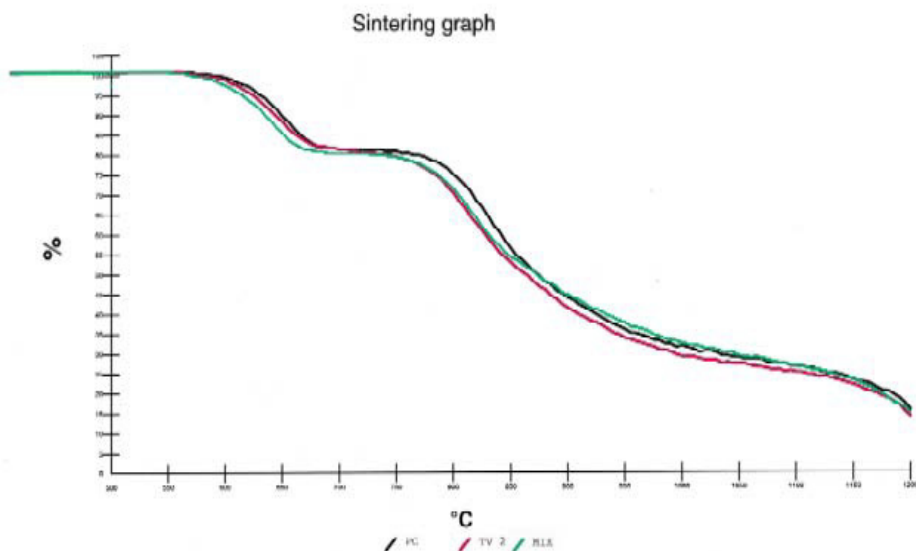


Figure 1. The sintering graph of EOL colour panel PC, TV and mix glasses in the temperature range 50-1200 °C

## PREPARATION OF THE TEST SAMPLES

### Clay bodies

The clay bodies were manufactured from three different earthenware clays. One of the clays was a Finnish earthenware clay from Koria (chemical composition given in the Table 3.), commercially used for the manufacturing of bricks. The same clay is also in use of studio scale tableware production of ceramics.

Danish VEDSTAARUP (ren rodler, firing range: 920-1040 °C) and German FUCHS KM (type: R, firing range: 1000-1200 °C) were used as references for the Finnish earthenware clay (firing temperature 1020 °C).

Table 3. Chemical composition of the Finnish earthenware clay, origin Korea.

Oxide	weight-%
SiO <sub>2</sub>	64.64
Al <sub>2</sub> O	15.50
TiO <sub>2</sub>	0.70
Fe <sub>2</sub> O <sub>3</sub>	5.89
CaO	2.26
MgO	1.76
Na <sub>2</sub> O	2.65
K <sub>2</sub> O	4.17
MnO	0.08
P <sub>2</sub> O <sub>5</sub>	0.16

Loss of ignition 1050 °C / 30 min = 2.31 %

The composition is calculated from the weight of dried clay.

After forming the clay samples were dried and bisque fired to the temperature 800°C. The firing curve used was according to the one given in the Table 4. with the exception of the reached temperature 800 °C.

### Manufacture of experimental clear glazes

The experimental glazes were prepared according to the normal glaze mixing process. Batches weighing 200 grams were mixed in water and ball-milled. Ball-milling time needed to grind the crushed glass the suitable particle size was selected from tests of varying ball-milling times from ½ hours to 10 hours. In these tests, a ball-milling time about two hours was found to give the best glazing properties and the best surface quality and the colour of the fired glaze. With longer ball-milling time the transparency of the glaze was decreased.

After milling the glazes were sieved and a suitable weight/litre ratio of the glaze was adjusted to the density of dipping glaze. The rheology of glaze suspension was adjusted by vinegar (5ml/400ml water). As a reference glaze commercial glaze for low firing, Ferro (VTR 102 [809640], firing range: 980°C - 1050°C), was used. Ferro VTR 102 – glaze contains lead oxide as a fluxing agent.

The glazes were applied by dipping the clay bodies to the glaze suspension. Each experimental glaze was dipped. The dipping was performed twice: half of the clay body was coated with once dipped layer and the other half with thicker, twice dipped glaze. The behaviour of the glaze during glazing was observed.

Test series, glazed with the CRT glass cullet glazes or the reference glaze, were fired with the same firing lay-out in order to avoid potential changes in the impact of the furnace atmosphere. The firing parameters used are shown at the Table 4.

Table 4. The firing parameters of the test samples coated with a glaze containing CRT glasses as the main raw material

100°C/h → 250°C  
150°C/h → 600°C  
200°C/h → 1020°C  
soaking in the temperature 1020°C 10 minutes

### **Manufacture of experimental coloured glazes**

In testing of the coloured glaze, the clay bodies were first coated with a white encope, applied by dipping to the test samples while still wet. The clay samples were dried and bisquit fired to 800 °C.

Seven different ceramic pigments belonging to different colour families, were chosen for test series. According to the results from testing colourless glazes, clear glaze with the best surface quality was chosen to a base glaze for testing the colouring properties. The glazing process was the same one used to colourless glazes. Batches weighing 200 grams were mixed after which 5 weight-% of colour pigments were added to the glazes. The batch was mixed in water and ball-milled for 2 hours. After milling the glazes were sieved and weight/litre ratio of the glaze was adjusted to the density of dipping glaze. The firing parameters were the same as for colourless glazes.

## **PROPERTIES OF THE FIRED GLAZED SURFACES**

### **Chemical durability**

Clossy glazes, i.e. glazes consisting mainly glassy phase, are known to be sensitive to alkalinen solutions. Chemical durability of the clear experimental glazes in an alkaline solution was tested by a standard procedure used in tile industry. The glazed test samples were exposed to a liquid 3% KOH solution for seven days. After this the surface of glazes was scratched with pencil and the marks left to the surfaces were analysed. The appearance of the surface after the exposure and scratching is used to classify the surfaces into five categories: AA (best), A, B (mark can be noted on the surface of the glaze), C, D (severely destroyed surface).

All the glazes could be classified into the best two categories, AA and A, for their alkaline resistance. Thus, all three CRT glasses give a similar alkaline resistance. This result is accordant with the similar composition of the glasses. However, it should be pointed out, that in this test series the possible content of heavy metals dissolved from the glazes was not measured.

### **Gloss of the clear glazes**

The surface quality of the glazes was studied also by measuring the gloss. 44 test samples with two different glaze thicknesses were analysed. The gloss values are given in their Mean Value (MV), Standard Deviation (STD) and Co-efficient of Variation (CV) in Table 5 .



Table 5. Gloss given as the Mean Value (MV), Standard Deviation (STD) and Co-efficient of Variation (CV) of the gloss measurements of glazes made out of PC, TV and mix EOL CRT glasses.

	MV	STD	CV	
<b>PC</b>	56.6-67.2	2.5-6.3	4.5-9.4	1 layer
	82,2-84.1	1.5-2.5	1.9-3.0	2 layers
<b>TV</b>	31.1-48.8	1.8-6.9	1.6-3.6	1 layer
	55.5-73.2	1.9-2.6	3.5-4.3	2 layers
<b>MIX</b>	49.7-72.2	1.7-5.9	3.4-6.4	1 layer
	71.9-75.6	0.7-2.6	0.8-3.6	2 layers
<b>REF.</b>	44.9 / 43,1	3.6 / 0.7	7.9 / 1.6	1 layer
	46.9 / 67.4	0.7 / 1.9	1.5 / 2.9	2 layers

The reference glaze containing lead has more glossy surface than the glazes containing EOL CRT glasses. Similar phenomenon has been reported when studying the replacement of lead in low firing glazes [3] Lead oxide is commonly known to be essential component for manufacture of glossy low fired surfaces [4].

### Colour measurements

The colouring of test glazes were compared visually (for test series see Appendix 1.), and photometrically in terms of colour coordinates. The colours of the test glazes were measured with Perkin Elmer Lambda 2 UV/VIS Spectrophotometer equipped with an integrating sphere. The colour was measured by using the light source D 65. The measured values are expressed as standard colour measuring system CIE Lab used in ceramic industry (see Table 6.)

Table 6. Averaged colour coordinates of the experimental glazes and the reference glaze as given by the standardised systems according to CIE-Lab (L: brightness, complementary colour axis; a: red-green [+a: red, -a: green] and b; yellow-blue [+b: yellow, -b: blue]) and Hunter-Lab.

	REF.	MIX	PC	TV		REF.	MIX	PC	TV
CIE LAB					Hunter LAB				
	LILAC 15090								
L*	63.70	62.99	55.69	60.31	L:	56.95	56.19	48.58	53.35
a*	12.03	7.76	8.71	8.24	a:	7.12	3.34	4.29	3.81
b*	-11.80	-11.93	-20.11	-16.36	b:	-6.49	-6.62	-14.54	-10.86
	LIGHT RED 27496								
L*	59.59	71.63	66.33	68.54	L:	52.60	65.65	59.79	62.22
a*	38.48	20.68	25.83	24.87	a:	32.29	15.40	20.21	19.39
b*	25.80	18.24	20.28	20.30	b:	19.57	17.58	17.92	18.33
	TURQUISE A 2005								
L*	72.94	77.76	75.62	77.35	L:	67.13	72.67	70.20	72.19
a*	-16.61	-8.33	-10.69	-9.25	a:	-18.07	-11.72	-13.51	-12.48

	REF.	MIX	PC	TV		REF.	MIX	PC	TV
CIE LAB					Hunter LAB				
b*	-10.39	-0.65	-2.68	-1.20	b:	4.49	4.11	2.20	3.60
BROWNISH RED 11690									
L*	43.91	56.00	54.72	57.28	L:	37.11	48.90	47.60	50.21
a*	31.08	22.98	25.49	22.57	a:	23.32	16.88	19.13	16.58
b*	16.69	15.64	17.33	15.30	b:	12.07	13.48	14.21	13.48
BLACK FK 4104									
L*	19.93	32.09	27.09	29.02	L:	17.24	26.69	22.64	24.17
a*	-0.55	-1.57	-1.59	-1.64	a:	-1.32	-2.59	-2.30	-2.45
b*	-9.38	-5.36	-6.82	-5.90	b:	-4.66	-1.79	-2.89	-2.22
BROWN 11156									
L*	22.27	31.98	26.33	29.52	L:	18.95	26.60	22.04	24.59
a*	2.45	3.10	1.72	3.12	a:	0.33	0.49	-0.23	0.57
b*	-6.82	-1.96	-3.77	-1.47	b:	-2.92	0.48	-0.87	0.68
BLUEISH VIOLET 15033									
L*	29.87	32.91	26.74	31.03	L:	24.87	27.38	22.36	25.82
a*	9.89	17.48	23.85	19.28	a:	5.17	10.89	15.36	12.16
b*	-27.40	-46.59	-47.26	-46.63	b:	-21.18	-45.96	-47.21	-46.06

The brightness of the colour hues decreases when no lead is present in the glaze composition. The most notable change in the colour hue can be detected with colour pigments giving a red and lilac-violet colour. Lilac-violet pigments are having more reddish hue in the reference glaze than in CRT containing glazes. A similar changes in colour hue related to the lead content has been discussed when colouring glasses [5].

### Testing of the glazes on tableware products

In addition to the flat clay surfaces, glazes were also tested on hand thrown products (see Figure 2.). The clay body used for the series of containers (sizes: Ø 60-85 mm, heights: 70-90 mm) was Finnish earthenware. Glazing of lids is similar to the process of test samples described in Chapter Test series for coloured glaze.

The behaviour of the test glazes in the production process was similar to the reference materials. The quality of the fired products was good with the exception of some glazing faults, with thicker glaze as normal thus causing hairline cracks.

## CONCLUSIONS

In this study test glazes containing 86-96% of cleaned and crushed EOL CRT glasses, TV, PC and mix, have been made and analysed. The firing properties of the glazes as well the surface properties of the final glaze surfaces have been masured.. Both the test results and visual look of test glazes indicate that CRT glasses can be used as a glaze material for low fired ceramics. The valuable properties of CRT glasses can be utilized to the full and can give a high value recycling for CRT glasses.



Figure 2. Products made by throwing out of Finnish earthenware and glazed with clear and coloured test glazes. Glazes contain 95 weight-% of EOL CRT glass.

Clear differences between the different glass sources, TV, PC and mix, could not be found. However, the glaze containing PC colour panel glass was the most stable when total manufacture process is taken to account. Out of the three clay bodies used in the test series Danish and German earthenwares were more tolerable to the changes in the thickness of glaze. On the test samples made out of Finnish earthenware a thick glaze tended to have some hairline cracks more easily than other clay bodies.

The suitability of the experimental composition for coloured glaze was tested by adding seven different ceramic pigments to the glaze suspension. The results showed that glaze body suits well for colouring purposes. The colour hue is to some extent depending on the chemical composition of the CRT containing glazes. Compared to the lead containing reference glaze the experimental CRT glass containing glazes have not the same gloss. The importance of lead oxide for the gloss and colouring of low fired glazes has been reported by other studies, too.

## ACKNOWLEDGMENTS

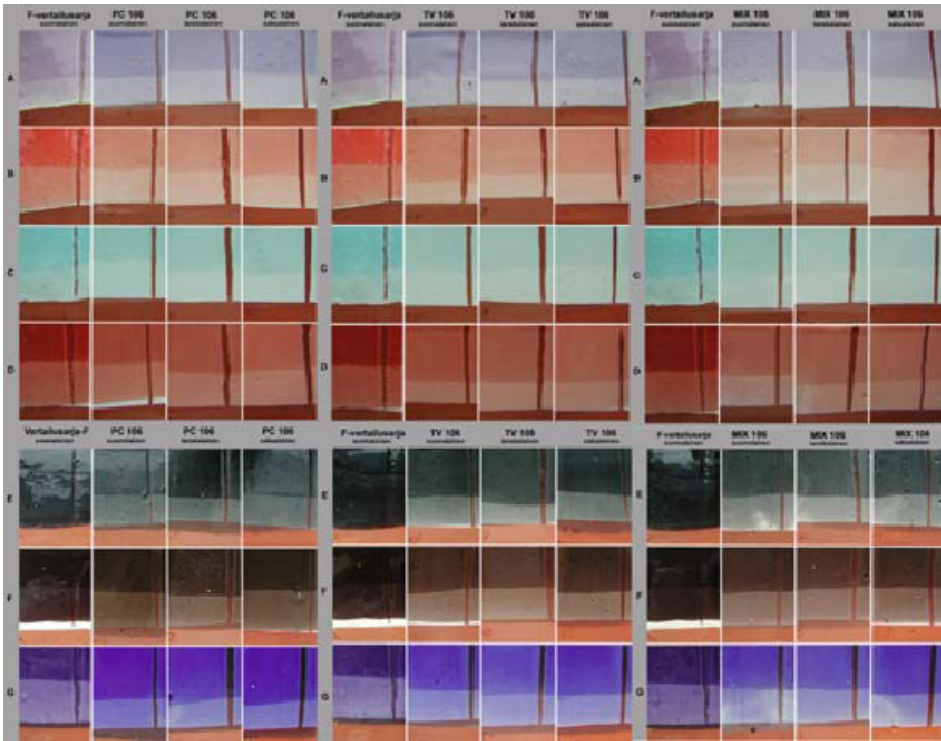
The author would like to thank Leena Hupa for her valuable comments on the manuscript. For this study, the primal open-loop recycling tests for low fired ceramics were carried out during a Brite/Euram project RECYTUBE (BE96-3661) and mainly during a Finnish national KIMOKELA project (Recycled Cathode Ray Tube Glass to a Raw Material for Finnish ceramic and glass industry) financed by National technology agency of Finland.

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APPENDIX 1.

Experimental coloured glazes containing TV, PC and mix EOL CRT glasses with addition of 5 weight-% of ceramic pigments. On the left clay body used is Finnish earthenware clay, series in the middle of the picture on the Danish Vedstaarup and on right the German Fuchs.





# Part II

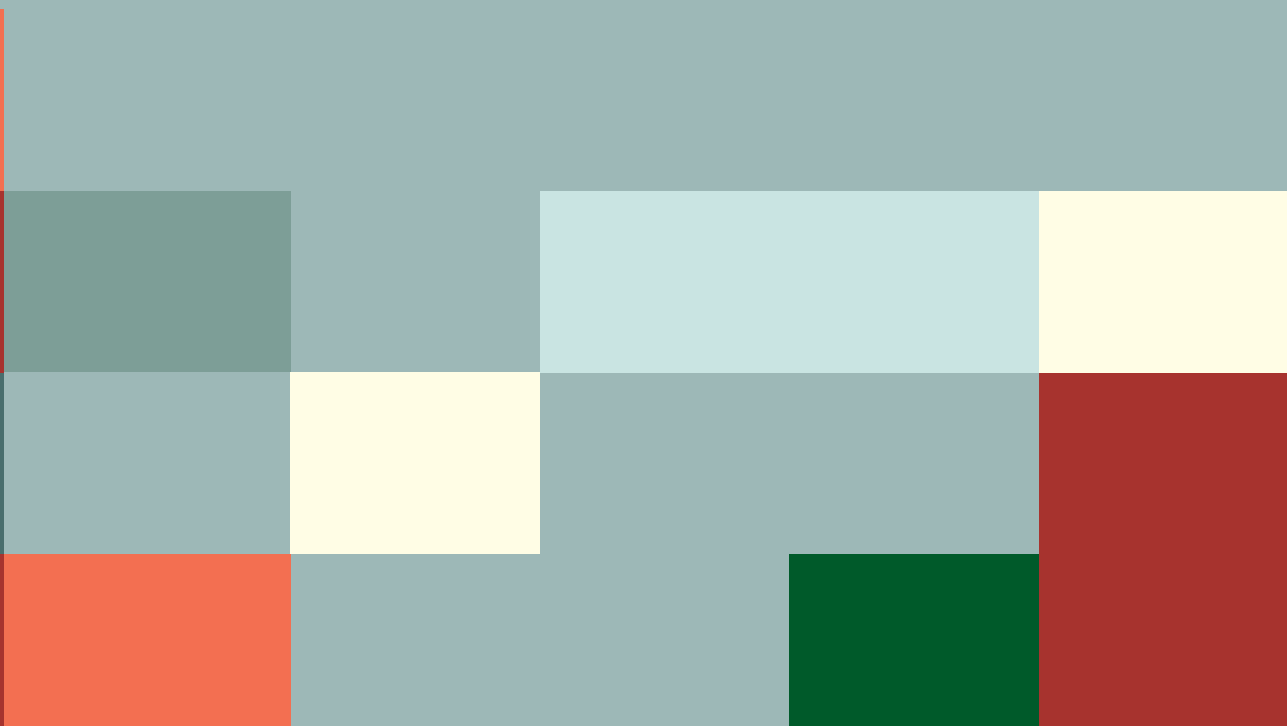
## Article V



**Raija Siikamäki**

# From Waste to Products

## – Utilisation of Glass Waste from TVs and PCs







# From Waste to Products

## – Utilisation of Glass Waste from TVs and PCs

### **Extended Abstract**

Everyone living in Finland generates up to 500 kilos waste annually. How is this fact related to design?

An ongoing research project at the Ceramics and Glass Department at University of Art and Design Helsinki (Uiah) aims at finding solutions to one of the waste flows, namely waste glass from TV and PC devices, cathode ray tube (CRT) glass. The study on recycling possibilities of CRT glass belongs to a wider waste management category, waste of electric and electronic equipment (WEEE), a topical issue in the EU. New European legislation aims at specifying the treatment and recycling responsibilities of this fast-growing waste stream.

## **Key responses to favour reuse and recycling**

Even if the material recycling has been identified to be one of the key issues in sustainable development, these are only a few legislative responses to promote material reuse and recycling. The most important ones, such as German ordinance on Packing Waste (1993), European Directive on Packing and Packing Waste (1994), European Landfill Directive (1999), European End of Life Vehicles Directive (2000) and Japanese Appliance Law (2001), all set responsibilities to the producers and/or retailers for waste recycling. Beside these responses in effect, a European WEEE Directive is being drafted. This Directive will classify WEEE to be treated separately from municipal waste. (European Commission, Flavin et al. 2002)

As materials, main types of municipal waste are packaging wastes of glass, plastics, paper and fibreboard and metals. The quantity of packaging materials used in Finland was 1.23 million tonnes in year 1998. Of this material flow 56 percent was recovered (through recycling or use as energy). Out of different material categories, highest rates of recovery were achieved for paper and glass: 72 and 62 percent, respectively. Packaging glass recycling has long traditions in comparison to recycling of other glass types. The recycling programmes for packaging glass operate nationwide. The composition of the material is relatively constant because of the manufacturing method. Consequently, industrial re-use is possible. Cathode Ray Tube glass is type of special glasses, manufactured from high-quality raw materials. A valuable, but at the same time problematic material, e.g. because of a need of multi-stage cleaning process, CRT glass comprises a wide range of chemical compositions. Chemical composition varies according to the type of device in which the CRT originates (TV, PC / Black& white, colour), manufacturer and the age of CRT. (Statistics Finland 2001, Kivipensas 2000)

## **KIMOKELA-project**

European Commission's RECYTUBE project, part of Commission's TRAWMAR (Targeted Reset Action of Waste Minimisation and Recycling) research program, was a background for this study project. The project partner in Finland was

Department of Ceramics and Glass at UIAH. During the two-year project, which ended in 1999, possible recovery technologies were found both for closed-loop and open-loop recycling. However, application areas were found to be dependent on local circumstances. (CREED 1999)

The aim of national KIMOKELA (Kierrätetty monitorilasi keramiikka- ja lasiteollisuuden raaka-aineksi), financed by the National Technology Agency, is to develop a safe and high quality technology for recycling CRT glass to raw material for Finnish ceramic and glass industry. This project aims at creating a network of co-operation that will be able to industrially produce high-quality raw material meeting the end-user's specifications. Project partners represent different parts of recycling chain.

For application areas in ceramic and glass industry, the technical work will consist of the following phases:

- to study the possible industrial applications for utilizing EOL CRT in Finnish ceramic and glass industry
- to specify the raw material requirements for each applications
- to evaluate the uncertain properties related to EOL CRT glass compositions
- to test the processed Secondary Raw Material (SRM) on laboratory scale
- to arrange the testing of SRM on industrial scale

The project is coordinated by UIAH. The partners are: Ekokem Oy Ab, Innolasi Oy, JL-Lasi, Kerapro Oy, Kuusakoski Oy, Tervatulli Oy and Wienerberger Oy.

## **Challenges for recycling**

Glass and ceramics production uses common but non-renewable natural resources. Beside reducing the waste material landfilled, new applications for open-loop recycling of glass materials can make considerable savings possible in the consumption of virgin raw materials and energy.

To find feasible applications for the utilisation of recycled materials is challenging: knowledge of material and production technologies is required as well sustained study. To introduce a new material to industrial manufacturing is a multistage process: the results of experimental work are evaluated in many phases.

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## Jätteestä tuotteiksi

### Tv- ja tietokonelaitteiden monitorilasin hyödyntäminen

**Jokainen meistä suomalaisista jättää jälkeensä lähes 500 kiloa jätettä<sup>1</sup> vuosittain. Miten tämä fakta liittyy muotoiluun?**

Taideteollisen korkeakoulun Keramiikka- ja lasisuunnittelun osastolla meneillään oleva Kierrätetty monitorilasi keramiikka- ja lasiteollisuuden raaka-aineeksi (KIMOKELA) -projekti pyrkii ratkaisuun yhden materiaalivirran osalta tätä ongelmakenttää. Monitorilasin kierrätys on yksi osa-alue laajemmassa sähkö- ja elektroniikkaromun (SER)<sup>2</sup> talteenotossa. Aihe on ajankohtainen; SER-jätteen käsittelyä ja kierrätystä koskeva EU-direktiivi on parhaillaan Euroopan Unionin komission käsittelyssä. Direktiivi tulee sisältämään painomääräisen kierrätysvelvoitteen, jonka täytyminen vaatii kuvaputkellisten laitteiden lasiosan kierrätyksen.

Tähän saakka suurin osa Euroopan sähkö- ja elektroniikkalaiteromusta on käsitelty tavallisen

yhdyskuntajätteen mukana. Samoin on tehty myös Suomessa, mutta vuoden 2002 alusta voimaan astunut muutos Ympäristöministeriön jäteluettelossa vaikuttaa romulaitteiden käsittelyyn. Uusi asetus määrittelee tv- ja tietokonelaitteiden kuvaputket ongelmajätteeksi niiden sisältämien ongelmajätteeksi luokiteltujen aineiden vuoksi. Laitteet eivät saa enää päätyä tavalliselle kaatopaikalle.

Materiaalien hyötykäyttö on yksi kestävän kehityksen avainalueista. YK:n vuonna 2000 hyväksymässä 2000-luvun julistuksessa *Millenium Declaration* asetetaan yhdeksi tärkeäksi taloudelliseksi tavoitteeksi ”rohkaista teollisuusmaiden raaka-aineiden kulutuksen leikkaamista kymmenesosaan”, tämänhetkisen tavoitteen ollessa neljäsosa. Tästä huolimatta maailmassa on hyväksytty viimeisenä kymmenenä vuotena vain muutamia säännöksiä, joilla on pyritty edistämään valmistusmateriaalien jälleenkäyttöä ja kierrätystä. (Katso taulukko 1.)

**Taulukko 1. Tärkeimpiä valmistusmateriaalien jälleenkäyttöä ja kierrätystä edistäviä säännöksiä**

Aika/ paikka	Säännös	Säännöksen sisältö tiivistelmänä
Saksa, 1993	Pakkausjätettä koskeva säännös	Valmistajien ja jakelijoiden on vastattava tuotepakkausten keräämisestä ja järjestettävä niiden uudelleenkäyttö tai kierrätys (tai liityttävä DSD-järjestelmään [kunnallista jätteiden keruuta vastaava järjestelmä] ).
EU, 1994	Direktiivi pakkauksista ja pakkausjätteestä	EU:n jäsenvaltioiden otettava talteen 50-65 % pakkausjätteestä, josta 25-45 % (pakkausmateriaalista riippuen) on kierrätettävä.
Japani, 1999	Laki pakkausten kierrättämisestä	Yritysten on otettava takaisin pakkaukset. Materiaalit, jotka eivät sovellu välittömästi kierrätettäväksi, on kerättävä, lajiteltava, kuljetettava ja kierrätettävä valmistajan kustannuksella.
EU, 2000	Direktiivi romuautoista	Valmistajien on otettava talteen ja jälleenkäytettävä romuautojen painosta 85 % vuoteen 2006 mennessä ja 95 % vuoteen 2015 mennessä.
Japani, 2001	Laki sähkölaitteista	Käytöstä poistetut televisiot, jääkaapit, pesukoneet ja ilmastointilaitteet on palautettava jälleenmyyjille tai keräilystä vastaaville viranomaisille kuluttajan kustannuksella. Laki sisältää kierrätysvelvoitteen (tv- ja ilmastointilaitteet: 55 % painosta, jääkaapit ja pesukoneet: vähintään 50 % painosta).

Näiden jo voimassa olevien säädösten lisäksi EU:n hallintoelimissä on parhaillaan työstettävänä sähkö- ja elektroniikkalaitteiden käsittelyä ja kierrätystä koskevat direktiivit. Yhdenmukainen tuotepoliittika (*Integrated Product Policy*, IPP) on keskeinen osa EU:n ympäristöasioita koskevaa kuudetta toimintaohjelmaa. IPP pyrkii erilaisin toimenpitein vähentämään jätteiden syntyä ja muita tuotteista aiheutuvia ympäristölle haitallisia vaikutuksia perusajatuksena elinkaariajattelua ja ympäristöasiat huomioivaa tuotesuunnittelua. Sähkö- ja elektroniikkatuotteet ovat ensimmäisiä tuoteryhmiä, joihin IPP:n mukaisia periaatteita sovelletaan EU:n lainsäädännössä. Valmisteilla ovat ns. WEEE-<sup>3</sup>, EEE-<sup>4</sup> ja ROHS-<sup>5</sup> direktiivit, jotka tulevat asettamaan vaatimuksia edellä mainittujen IPP:n periaatteiden lisäksi myös sähkö- ja elektroniikkaromun keräyksele sekä materiaalien käsittelylle ja kierrätykselle.

Sähkö- ja elektroniikkalaiteromu on EU:n alueella tällä hetkellä nopeimmin kasvava jätevirta: sen määrän arvioidaan lisääntyvän 3-5 prosentilla vuodessa eli arvion mukaan jätemäärä lähes kaksinkertaistuisi seuraavan kymmenen vuoden aikana. Tällä hetkellä SER:ä syntyy vuosittain noin 16 kiloa kuluttajaa kohden.

SER-jätteen käsittely tavallisena yhdyskuntajätteenä aiheuttaa haitallisia ympäristövaikutuksia laitteiden sisältämien raskasmetallien<sup>6</sup> ja halogeenoitujen aineiden<sup>7</sup> vuoksi. Lisäksi menetetään suuri määrä raaka-aineita, jotka olisi laitteiden esikäsittelyn jälkeen mahdollista hyödyntää. Raaka-aineiden säästymisen lisäksi voitaisiin samalla vähentää neitseellisten raaka-aineiden kulutusta.



## MITÄ OVAT YHDYSKUNTAJÄTE JA ONGELMAJÄTE

Jätehuoltomääräyksissä tarkoitetaan yhdyskuntajätellä asumisessa syntynyttä jätettä sekä ominaisuudeltaan, koostumukseltaan ja määrältään siihen rinnastettavaa teollisuus-, palvelu- tai muussa toiminnassa syntynyttä jätettä lukuun ottamatta ongelmajätettä. Materiaaleina yhdyskuntajäte koostuu paperista, altopahvista, metalleista, muoveista, pahvista ja biojätteestä. Lisäksi kertyy erilaisia haitallisia aineita ja ongelmajätettä, jotka vaativat erikoiskäsittelyn.

Suomessa kerätään yhteensä 2,5 miljoonaa tonnia yhdyskuntajätettä vuosittain. Tästä kokonaismäärästä pystytään hyödyntämään noin kolmannes; hyötykäytöksi luetaan käyttö sekä raaka-aineena että energiana. Hyötykäyttöasteet vaihtelevat suuresti materiaaleittain. Esimerkiksi pakkausmateriaalien (lasi, muovi, paperi/kuitu, metalli) sekä uudelleen käyttö että kierrätysaste ovat suhteellisen korkeita. (Katso taulukko 2.)

Pakkausmateriaaleja kulutettiin Suomessa vuonna 1998 yhteensä 1,23 miljoonaa tonnia. Tästä kokonaismäärästä pystyttiin hyödyntämään 56 prosenttia. Materiaaleina paperi ja lasi saavuttivat korkeimmat hyötykäyttöasteet: paperia hyödynnettiin 72 prosenttia ja lasia 62 prosenttia. Vastaavasti muovien ja metallien kohdalla hyödynnetään vain alle viidennes jätemateriaalien määrästä.

Suomessa kaatopaikkasijoitus on yhä ratkaisu vuosittain noin 10 miljoonan tonnin materiaalin



**Kuvat 1-2.** Kierrätyksestä palautuneita tietokonelaitteita ja kuvaputkia muoviosien poistamisen jälkeen.

**Taulukko 2. Pakkausmateriaalien uudelleenkäyttö ja hyödyntäminen Suomessa vuosina 1997 ja 1998 (Kivipensas, 2000)**

Pakkaus- materiaali	Pakkauksia (tonnia)		Uudelleen- käyttö (%)*		Pakkausjätettä (tonnia)		Kierrätetty (%) **		Hyödynnetty (%) ***	
	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
Lasi	378500	349900	87	85	52000	55700	48	62	48	62
Muovi	294100	306400	69	70	90000	89400	10	10	22	20
Paperi/kuitu	256800	257600	5	5	243500	246000	57	57	73	72
Metalli	239400	319100	86	90	31000	32000	8	16	8	16
<b>Yhteensä</b>	<b>1168800</b>	<b>1233000</b>	<b>64</b>	<b>66</b>	<b>416500</b>	<b>423100</b>	<b>42</b>	<b>45</b>	<b>54</b>	<b>56</b>

\* Uudelleenkäytöllä tarkoitetaan pakkauksen käyttämistä alkuperäiseen tarkoitukseen

\*\* Kierrätyksellä tarkoitetaan jätteen hyödyntämistä materiaalina

\*\*\* Hyödyntäminen sisältää kaikki jätteen hyödyntämistavat (kierrätyksen, polton ja kompostoinnin)

(Lähde: Suomen ympäristökeskus/ympäristökuormitusyksikkö; Pakkausalan ympäristörekisteri PYR; Pakkausteknologiaryhmä ry PTR)

jätteenkäsittelyssä (määrä koostuu teollisuuden jätteistä ja yhdyskuntajätteistä). Määrä on suuri ja eurooppalaisessa vertailussa Suomi sijoittuikin suurten teollisuusmaiden joukkoon laskettaessa jättekertymää/kansalainen (Tilastokeskus, 2001).

Jäte luokitellaan ongelmajätteeksi, jos sillä on jokin vaarallinen ominaisuus (esim. räjähtävyys, syttyvyys, myrkyllisyys, tartuntavaarallisuus tai ärsyttävyys). Ongelmajäte voi olla vaarallinen ympäristölle tai lisääntymiselle vaurioittaen perimää. Ongelmajätteisiin kuuluvat vuoden 2002 alusta alkaen muiden muassa käytöstä poistettut sähkö- ja elektroniikkalaitteet, joista ei ole poistettu vaarallisia osia, romuajoneuvot, nestekidenäytöt, vanhojen kylmälaitteiden freonipitoiset kylmäaineet ja eristeet.

Uusi jäteluettelo sisältää 404 nimikettä, jotka luokitellaan ongelmajätteeksi. Tämä määrittely lisää jätteen haltijan velvoitteita: ongelmajätteen käsitteijä tarvitsee toimintaansa ympäristöluvan, käsitteilylle on jätelainsäädännössä asetettu velvoitteet ja pakkaamista ja kuljetusta koskevat määräykset (Ympäristönsuojelulaki 2000, Ympäristösuojeluasetus 2000, Valtioneuvoston päätös 1996). Uusi luokittelu lisää arvioiden mukaan Suomessa vuosittain syntyvän ongelmajätteen kokonaismäärää noin 500 000 tonnista 800 000–1 000 000 tonniin (Ympäristöministeriö, 2001).

Määrien jatkuvasti kasvaessa jätteen synnyn ehkäisy on muodostumassa yhä tärkeämmäksi tavoitteeksi maailmanlaajuisesti jätehuollossa. Esimerkkinä tällaisista pyrkimyksistä voi mainita australialaisen Canberran kaupungin vuonna 1996 asettaman tavoitteen tulla jäteteettömäksi kaupungiksi vuoteen 2010 mennessä. Tämä kaupungin ensisijaiseksi tavoitteeksi ilmoittama ”waste free society” määri-

tellään suunnitelmassa seuraavasti: *“A waste free society is one in which no material is regarded as useless. Where all resources find another application or useful function.”* Samansisältöisiä tavoitteita on asetettu myös esimerkiksi Kanadan ja Uuden-Seelannin (*Zero Waste Principle*) paikallishallinnoissa.

#### MIKSI HYÖDYNTÄÄ JÄTTEITÄ KERAMIikka- JA LASITUOTTEISSA?

Keramiikassa ja lasissa käytettävät raaka-aineet ovat yleisiä luonnosta löytyviä materiaaleja, mutta kuitenkin uusiutumattomia luonnonvaroja, joiden käyttö raaka-aineena vaatii puhdistusprosesseja. Jättemateriaaleja käyttäen vähennetään puhtaiden raaka-aineiden kulutusta ja samalla kaatopaikattavan jätteen määrää. Keramiikan ja lasinvalmistuksen menetelmät ovat korkeita lämpötiloja vaativia prosesseja: keramiikan polttolämpötila on keraamisesta massasta riippuen noin 1000–1350 °C, lasin sulatustemperatuurit vaihtelevat lasimassan koostumuksen mukaisesti noin 1200–1500 °C. Näissä lämpötiloissa on mahdollista saada monet jättemateriaalit sitoutumaan peruskoostumukseen siten, että materiaalit ovat liukenemattomassa muodossa. Kierrätetyn materiaalin käytöllä on myös etuja, joita tuo mukanaan jo poltto- tai sulatusprosessin läpikäynyt materiaali, esimerkiksi lasinsulatuksessa kuluvan energian määrä vähenee käytettäessä kierrätettyä materiaalia.

On mielenkiintoista verrata pakkauslasin ja monitorilasin kierrätystilannetta Suomessa. Pakkauslasin uusiokäyttö ja kierrätysjärjestelmä toimivat

erinomaisesti: lasipakkauksista palautui uudelleen- käyttöön 85 prosenttia vuonna 1998 ja niistä hyöty- kättiin 62 prosenttia samana vuonna (katso tau- lukko 2). Järjestelmä on vakiintunut ja toimii maan- kattavasti. Materiaali erotellaan kirkkaaseen ja vä- rilliseen fraktioon. Tämä mahdollistaa automaattisen puhdistus- ja murskausjärjestelmän, johon voidaan soveltaa materiaalin optista erottelua. Pakkauslasi on jo valmistusmenetelmänsä vuoksi koostumuk- seltaan melko tasalaatuista, joten sen teollinen hyö- tykäyttö on mahdollista. Suomessa toimii sekä pak- kauslasia että lasivillaa valmistavaa teollisuutta, jotka hyödyntävät tuotannossaan kierrätysmateriaa- lia. Suomessa kierrätetään myös osa tasolasijätteestä ja laminoitua lasia, jota palautuu autojen tuuli- laseista.



**Kuva 3.** Lasinmurskausta Suomen Uusioaines Oy:llä.

Kuvaputkellisten laitteiden sisältämä lasi eroaa materiaalina monessa suhteessa pakkauslasista. Lasi on huomattavasti korkealaatuisempaa kuin pak- kauslasi, esimerkiksi valmistuksessa käytetyt mate- riaalit ovat puhtaampia. Lisäksi monitorilasi sisältää monia erittäin arvokkaita raaka-aineita (mm. harvi- naiset maametallit). Samanaikaisesti materiaali on ongelmallista lasimateriaalia. Monitorilasiens koos- tumukset vaihtelevat suuresti: pelkästään jokainen yksittäinen laite sisältää kahta eri lasikoostumusta. Lisäksi koostumus vaihtelee laitetyypin (tv-laite, tietokone/ mustavalkonäyttö, värinäyttö), valmista- jan ja valmistusajankohdan mukaan. Tekniset muo- tokset kuvaputkessa vaikuttavat aina myös siinä käytettävään lasimateriaaliin. Monitorilasin hyöty-

käyttö vaatii aina monivaiheisen puhdistusprosessin. Tämä aiheuttaa kustannuksia, jotka tekevät materi- aalista hintaluokaltaan pakkauslasia kalliimpaa.

Monitorilasin mahdolliset hyötykäyttökohteet eroavat pakkauslasin hyötykäytöstä. Tällä hetkellä kaikki Suomesta hyötykäyttöön ohjautuva materiaa- li, joka on arvioiden mukaan noin 10–15 % palautu- vien laitteiden sisältämästä monitorilasin kokonais- määrästä, viedään maasta. Monitorilasimateriaalin ainoa teollisen mittakaavan hyötykäyttö on ollut suljettu kierto, jolloin materiaali käytetään uudelleen monitorien valmistamiseen. Lasin koostumukseen liittyvistä syistä tähän tarkoitukseen on soveltunut ainoastaan 1/3 kierrätysmateriaalista. Monitoreiden valmistusprosessiin voidaan lisätä vain osa kierrä- tysmateriaalia, maksimissaan 40–50 %. Näin ollen suljettu kierto voi parhaimmillaankin hyödyntää vain pienen osan kuvaputkellisten laitteiden lasi- määrästä. Käyttö suljetussa kierrossa on Suomessa mahdotonta, sillä täällä ei ole monitoreja valmista- vaa teollisuutta. Materiaalin hyödyntämistä vaike- uttaa myös se, että koko kierrätysjärjestelmä ja sen kustannusten jakaminen ovat vielä hakemassa muotoaan.



#### KIMOKELA-PROJEKTI

Euroopan mittakaavassa monito- rilasin kierrätystä ja hyötykäyttö- mahdollisuuksia on tutkittu Euroopan komission TRAWMAR (*Targeted Reset Action of Waste Mi- nimisation and Recycling*) tutkimusohjelmaan kuu- luvassa projektissa RECYTUBE (*Integrated recy- cling of End-of-Life Cathode Ray Tube Glass*). Suomesta mukana tutkimustyössä oli Taideteollisen korkeakoulun Keramiikka- ja lasisuunnittelun osas- to.

Kaksivuotinen projekti päättyi vuonna 1999. Mahdollisia hyötykäyttökohteita löytyi, mutta ne vaihtelevat kuitenkin eri maissa, sillä keräilymene- telmä vaikuttaa kierrätetyn materiaalin koostumuk- seen ja sen vaihteluväleihin. Myös palautuvien lait- teiden käyttöikä vaihtelee eri maissa. Lisäksi lasia hyödyntävän teollisuuden tuotantomenetelmät ovat erilaisia eri maissa, ja korvattaessa neitseellisiä raaka-aineita kierrätysmateriaalilla paikallinen raa- ka-aineiden hinta vaikuttaa siihen, mitkä sovellutus- alueet ovat mahdollisia.

RECYTUBE-projektin tulokset ovat olleet tausta- na lähdeittäessä etsimään väyliä monitorilasimateri- aalin käytölle suomalaisessa keramiikka- ja lasialan



teollisuudessa hyödyntäen jättemateriaalin ominaisuuksia. Kansallisen KIMOKELA-projektin tavoitteena on selvittää kierrätetyn monitorilasin kierrätysetku alkaen laitteiden keräilystä puhdistuksen ja murskauksen kautta raaka-aineeksi teollisuudelle. Työ kartoittaa mahdolliset sovellutusalueet suomalaisesta teollisuudesta ja luo yhteistyöverkoston, joka pystyy valmistamaan teollisesti hyödynnettävissä olevaa raaka-ainetta kierrätetystä monitorilasista ja yhteydet keramiikka- ja lasialan materiaalin loppukäyttäjiin.

Kooltaan lasiosa on televisio- ja tietokonenäyttöissä suurin yksittäinen osa: kuvaputkellisten laitteiden kokonaispainosta 60-70 % on lasia. Kaiken kaikkiaan käytöstä palautuvan monitorilasin määräksi Suomessa ja koko Euroopassa vuosina 2000-2003 on arvioitu taulukon 3. mukaiset tonnimäärät.

**Taulukko 3. Arvio kierrätyksestä palautuvan monitorilasin määrästä Suomessa ja Euroopassa vuosina 2000-2003**

	2000	2001	2002	2003
Suomi	3 600	3 900	3 900	4 100
Yhteensä Euroopassa (tonneja)	260 000	250 000	275 000	280 000

Arvio perustuu seuraaville olettamille:

	Keskim. käyttöikä (vuosia)	Keskim. paino (kg)	Monitorilasin määrä (kg)
Televisiot	12	24,3	11
Tietokoneet	8	10,6	3,8

Lähde: Creed (Centre de Recherches et d'essais pour l'environnement et le Déchet) 1998, painamaton lähde.

Projektin tavoitteena on ohjata kotimaiseen hyötykäyttöön 2/3 taulukon 3. mukaisesta Suomesta kerättävästä monitorilasimateriaalista. Kolmannes materiaalista on koostumuksensa vuoksi mahdotonta hyödyntää kotimaisessa teollisuudessa.

#### KIERRÄTETYN MATERIAALIN HYÖTYKÄYTTÖ SUOMESSA

Jotta mahdollisimman suuri osa kierrätysmateriaalista voidaan hyödyntää, loppukäyttäjää

tarvitaan sekä keramiikka- että lasiteollisuuden parista ja näiden teollisuudenalojen sisällä erilaisista tuotantoprosesseista. Tällöin erilaiset kierrätysmateriaalin koostumusvaihtoehdot ja puhdistus- ja murskausprosessissa syntyvät eri partikkelikoon erät saadaan käyttöön.

Keraamisissa tuotannossa monitorilasimateriaalia on mahdollista hyödyntää lasiteen osaraaka-aineena. Tällöin on mahdollista korvata lasilla frittien eli sulatteiden käyttöä. Suomessa ei tällä hetkellä valmisteta frittejä keraamiselle teollisuudelle. Lasi-tuotannossa monitorilasia voidaan hyödyntää joko osaraaka-aineena korvaamaan neitseellisten raaka-aineiden käyttöä tai tiettyjen valmistustekniikoiden osalta tuotanto voi perustua kokonaan kierrätysmateriaalin käyttöön.

Tutkimustyö jakautuu viiteen päävaiheeseen:

1. Sovellusalueiden kartoitus
2. Puhdistus- ja murskausprosessien optimointi
3. Kuvaputkilasin kemiallisen koostumuksen vaihtelun kartoittaminen
4. Laboratoriomittakaavan koetuoanto
5. Tuotantomittakaavan kokeet

Jotta materiaalin teolliset sovellutusalueet voidaan kartoittaa, tarvitaan arvio kierrätetyn materiaalin koostumusvaihteluista. Niiden arviointi edellyttää sekä kerättävien erilaisten näyttöpäätteiden suhteellista osuutta että erilaatuisten näyttöjen koostumusvaihteluita. Eri sovellutusalueiden sallima vaihtelu materiaalin koostumuksessa määrittää puhdistettavan erän minimikoon. Puhdistus- ja murskausprosessien optimointi tapahtuu sovellutusalueiden asettamien rajojen mukaisesti perustuen koostumus-analyysihin kierrätysmateriaalin kemiallisesta koostumuksesta ja puhtausasteesta.

Koostumusanalyysihin perustuen tarkennetaan eroteltavat luokat ja se, miten tarkoin on lajiteltava ja miten suuri vaikutus koostumukseen on esimerkiksi palautuvan laitteen iällä. Sovellutusalueiden laatuvaatimusten mukaisesti suunnitellaan lasin murskausprosessi. Tärkeimpinä osa-alueina murskausprosessissa ovat: a) tavoitellun raekokajakau-man saavuttaminen ja b) mahdollinen puhdistus murskauksen jälkeen.

Materiaali seulotaan tarvittaviin raekokoihin. Esitutkimuksen perusteella tiedetään, että lasimateriaalia tullaan tarvitsemaan minimissään kolme eri raekokoluokkaa. Laboratoriomittakaavan kokeiden tuloksiin perustuen toteutetaan teollisen mittakaavan tuotantokokeet yhteistyöyrityksissä.

## YHTEISTYÖOSAPUOLET

Projektin yhteistyösapuolet edustavat monitorilasin keräily-, kierrätys- ja hyötykäyttöketjun eri vaiheita.

Monitorilasin keräilijöitä edustavat projektissa Kuusakoski Oy ja Tervatulli Oy. Kuusakoski Oy käsittelee SER-jätettä ja on maailmanlaajuisesti toimiva metallin kierrätysyhtiö, joka jalostaa metalliromua raaka-aineeksi teollisuudelle. Tervatulli Oy on Oulussa toimiva vuonna 1997 perustettu niin kutsuttu sosiaalinen yritys. Yrityksen omistaa Oulun Kuurojen Yhdistys ry. Yrityksen ympäristöpaja vastaanottaa kodinkoneita, ATK-laitteita ja lasia.

Ekokem Oy Ab ja Suomen Uusioaines Oy edustavat projektissa kierrätysmateriaalin puhdistuksen ja murskauksen osaamista. Ekokem Oy kehittää kuvaputkilasin teollisuusmittakaavan puhdistus-, murskaus- ja sekoitusprosessit. Yritys osallistuu tutkimushankkeeseen yksityisenä rahoittajana ja panostaa myös omia resurssejaan tutkimushankkeen toteuttamiseen. Yritys rakentaa televisioiden ja monitorien purkuprosessin Riihimäelle, jossa kuvaputkilasiraaka-aineen tuotanto tapahtuu tuottaen tutkimuksessa tarvittavan kuvaputkilasiraaka-aineen, joka erotetaan kotimaassa kerätyistä televisioista ja monitoreista. Ekokem Oy käsittelee purkuprosessissa syntyvät jätteet. Forssassa toimiva Suomen Uusioaines Oy kerää, ottaa vastaan ja käsittelee valtaosan Suomessa hyötykäyttöön menevästä keräyslasista. Tällä hetkellä yrityksessä käsiteltävä lasimateriaali on pakkauslasia ja sekä laminoimatonta että laminoitua tasolasia. Yritys suorittaa materiaalin testiajoja hankkeen aikana. Jatkossa yrityksen tavoitteena on toimia monitorilasimateriaalin käsitteijänä tuotantomittakaavassa.

Materiaalin loppukäyttäjää projektissa edustavat Innolasi Oy, JL-lasi, Kerapro Oy ja Wienerberger Oy. Innolasi Oy valmistaa kierrätetystä pakkauslasista rakennuselementtejä ja projektissa mukanaolon toivotaan laajentavan yrityksen tuotevalikoimaa. JL-lasi edustaa studiolasituotantoa. Tämän sovellutusalueen tuotantomittakaavan kokeet toteutetaan yrityksessä. Kerapro Oy on vuonna 1999 perustettu keramiikka-alan maahantuoja ja jälleenmyyjä, joka pyrkii tuotevalikoimansa laajentamiseen hyödyntäen kierrätysmateriaalia. Wienerberger Oy on monikanallinen yritys, joka omistaa Suomessa muun muassa poltettujen tiilien tuotantoon erikoistuneet tehtaat Koriolla ja Lappilassa.

Edellä mainittujen yritysten lisäksi projektissa ovat mukana SET Sähkö-, elektroniikka- ja tietote-

ollisuus-liitto, joka on Suomessa toimivan elektro-



**Kuva 4.** Kuvaputken eri osien erottelua ja puhdistusta.

niikka- ja sähköalan toimialajärjestö. Kunnallista näkökulmaa työhön tuo Riihimäen kaupunki, joka tunnetaan nimenomaan lasinvalmistuksesta. Yhteistyöyrityksistä kaksi sijaitsee Riihimäellä ja kaupunkiin on tarkoitus saada paikallinen materiaalin käsittely-loppukäyttäjä -ketju.

Keramiikka- ja lasisuunnittelun osasto Taideteollisessa korkeakoulussa vastaa sovellutusalueiden kartoituksesta suomalaisessa keraamisessa ja lasiteollisuudessa ja materiaaalilta vaadittavien ominaisuuksien kartoituksesta eri sovellutusalueilla. Siellä suoritetaan myös laboratorioskaalan koetuantanto eri sovellutuksista ja TaiK järjestää tuotantomittakaavan kokeet yhteistyöyrityksissä.

Kaksivuotista (vuodet 2001-2002) tutkimushanketta rahoittavat TEKESin tutkimusohjelma STREAMS (Yhdyskuntien jätevirroista liiketoimintaa) ja yhteistyöyritykset.

## JÄTEMATERIAALIN HYÖDYNTÄMISEN HAASTEITA

Jo pelkästään kierrätyksestä palautuvan materiaalin määrä tuo mukanaan suuria haasteita. Tämä määrittelee myös paljon sovellutusalueita: materiaalin tarjonnan ja kysynnän tulee kohdata siten, että erilaisille koostumuksille löytyy hyötykäyttö. Kierrätysketjun ollessa vasta muovautumassa maassamme, tutkimustyö on mukana muovaamassa sen organisoitua.

Monitorilasin hyödyntäminen, kuten jätteiden hyödyntäminen laajemminkin, vaatii materiaalin ja

valmistusprosessien hyvää tuntemusta. Vain tällä edellytyksellä on mahdollista löytää ne kohteet, jotka pystyvät hyödyntämään jättemateriaaleja jätteen ominaisuuksia hyväkseen käyttäen. Työ vaatii pitkäjännitteisyyttä: uuden materiaalin tuominen teolliseen valmistusprosessiin on monivaiheinen tutkimustyö, ja ennen kuin uusi tuote on markkinoilla, kokeellisen työn tuloksia mitataan eri vaiheissa.

Jätteiden hyödyntäminen on tärkeä osatekijä kestävässä kehityksessä ja luonnonvarojen kestävässä käytössä. Aihe on ajankohtainen ja tärkeä tutkimuskysymys, koska elintärkeiden luonnonvarojen säilyminen ennallaan ei ole meille itsestään selvyyttä. Kestävä kehitys on jatkuva oppimis- ja määrittelyprosessi, jossa pyritään vastamaan luonnon monimuotoisuuden ja yhteiskunnan moniarvoisuuden haasteisiin. Tutkimuksen avulla voidaan tuoda konkreettisuutta ja käytännönläheisyyttä tähän termiin, joka tuntuu abstraktilta ja on siten helposti sivuutettavissa.

## VIITTEET

1. Jäte: esine tai aine, jonka sen omistaja on poistanut tai on velvoitettu poistamaan käytöstä.
2. SER-jäte koostuu kodinkoneista, ATK-laitteista, televisioista, viestintälaitteista, sähköisistä käsityölaitteista, keskus- ja siirtojärjestelmistä, mittaus- ja säätölaitteista ja sairaala- ja laboratoriolaitteista.
3. WEEE-Directive: Directive of the European parliament and of the council on waste electrical and electronic equipment (Euroopan parlamentin ja neuvoston direktiivi sähkö- ja elektroniikkalaiteromusta).  
Ehdotukset kokonaisuudessaan on löydettävissä osoitteesta: [http://europa.eu.int/eur-lex/fin/com/pdf/2000/fin\\_500PC0347\\_02.pdf](http://europa.eu.int/eur-lex/fin/com/pdf/2000/fin_500PC0347_02.pdf)
4. EEE-Directive: Directive of the European Parliament and of the Council on the impact on the environment of electrical and electronic equipment (Euroopan parlamentin ja neuvoston direktiivi sähkö- ja elektroniikka laitteiden ympäristövaikutuksista).
5. ROHS-Directive: Directive of the European Parliament and of the Council on the restriction of the use of certain hazardous substances in electrical and electronic equipment (Euroopan parlamentin ja neuvoston direktiivi tiettyjen vaarallisten aineiden käytön rajoittamisesta sähkö- ja elektroniikkalaitteissa).
6. Ympäristön kannalta ongelmallisimpia SER-jätteen sisältämiä raskasmetalleja ovat elohopea, lyijy, kadmium ja

kromi.

4. Halogeenidut aineet, kuten kloorifluorihiilivedyt (CFC), bromatut palonestoaineet, polyklooratut bifenyylit (PCB) ja polyvinyylikloridi (PVC)

5. "Zero Waste is a philosophy and a design principle for the 21st Century. It includes 'recycling' but goes beyond recycling by taking a 'whole system' approach to the vast flow of resources and waste through human society. Zero Waste maximizes recycling, minimizes waste, reduces consumption and ensures that products are made to be reused, repaired or recycled back into nature or the marketplace". The grassroot recycling network

[http://www.grn.org/zerowaste/zerowaste\\_faq.html](http://www.grn.org/zerowaste/zerowaste_faq.html)

## KIRJALLISUUS

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