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# Leaded Glass from Cathode Ray Tubes (CRTs)

A Critical Review of Recycling and Disposal Options



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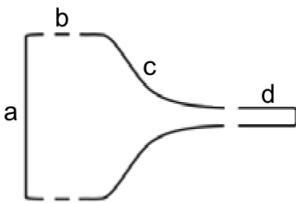
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### Abstract

As a result of the replacement of cathode ray tube screens (CRTs) by flat screens, the world is confronted with stranded end-of-life CRTs. CRTs contain 1 to 1.5 kg of lead per screen; mainly found in the funnel and neck glass for radiation protection purposes. The lead content makes this CRT glass unsuitable in most glass applications. Thus, there is an urgent need for alternative recycling options that are able to use up the CRT leaded glass while safely retaining the lead out of contact with humans and the environment. We provide a critical review of products in which CRT leaded glass can replace raw materials. Additionally, we review current disposal options. The main focus of the review is the fate of lead in the new products and repositories. The results complement available evaluations of the technical feasibility and direct environmental impacts of the options.

## 1. Introduction

The major constituent of a cathode ray tube screen (CRT) is glass. Most of this glass is made of a barium-strontium mix, similar to the one used for container glass [1]. However, about 35% of the CRT glass, specifically the funnel and neck glass contains lead oxide (PbO) [1]–[4]. The PbO content is 11% to 28% the mass of the leaded CRT glass. Figure 1 sketches a CRT and the different types of glasses that it comprises.



**Figure 1: Sketch of a CRT screen.** a) frontal glass or panel glass, b) glass frit, c) funnel glass, d) neck glass. b, c and d contain PbO.

As a result of a technological replacement, the recycling of CRT glass into new CRTs is no longer possible [6]. Large amounts of end-of-life CRT must therefore be recycled into other products or disposed of. The recycling or disposal of the CRT leaded glass is of particular concern as the high PbO content makes the glass unsuitable for most current glass applications [7].

Lead is a toxic heavy metal, which causes adverse effects to human health when inhaled or ingested [5]. The Provisional Tolerable Weekly Intake (PTWI) for lead determined by the Joint Food and Agriculture/World Health Organization Expert Committee on Food Additives (JECFA) has been dropping since a first lead toxicity assessment in 1972. In accordance with new scientific evidence relating lead to irreversible health damages in humans, currently, the JECFA declares that it is not possible to establish a PTWI for lead that would be considered health protective [5].

Given the quantities of the toxic metal lead in CRT leaded glass and the shrinking lead exposure limits, an updated review of the recycling routes in which CRT leaded glass is used in other products, with a particular focus on the fate of lead during use, is necessary.

In this contribution, we carry out a critical review of eight recycling options for CRT leaded glass found in publicly available literature. We make a rough estimation of the potential amounts of CRT leaded glass that could be used in other products and identify whether the usage of lead is indispensable in each case. The potential lead leaching during use of the products is also compiled from available literature. Disposal options currently used in Europe and the United States are also reviewed.

The results of this critical review complement existing evaluations of recycling options regarding technical feasibility and direct environmental impacts, such as the ones carried out by Xu and colleagues in 2013 [7] and Huisman in 2004 [8]. The criteria considered support preliminary feasibility assessments of current and future recycling and disposal options for CRT leaded glass.

## 2. Methodology

Based on the chemical composition of CRT leaded glass, we identified products in which the glass could be used as replacement for raw materials. Information about the technical feasibility of material replacements in the identified products was obtained from publicly available scientific studies and industry reports.

The literature was reviewed under the following guiding principles:

1. A new product in which the CRT leaded glass is used must require the properties of lead, not only enclose it. This is in accordance with the European Waste Framework Directive [9].
2. Lead is a toxic heavy metal; lead leaching during use of the new products must be in accordance with permitted human intake values.
3. Lead must be retrievable at the end of life of new products to ensure that it can be properly disposed of.

These principles were translated into four review criteria is presented below.

1. **Potential global demand for CRT leaded glass.** CRT leaded glass may be used as raw material in the manufacturing of other glass products or as source for lead metal. The potential global demand for CRT leaded glass  $D_{CRTi}$ , in mass units, was calculated with Equation 1 for glass replacements and with Equation 2 for lead metal replacements.

$$D_{CRTi} = w_{CRTxi} \times w_{xi} \times G_i \quad \text{Eq 1}$$

Where  $w_{CRTxi}$  is the mass fraction of material  $x$  in product  $i$  replaced by CRT glass,  $w_{xi}$  is the mass fraction of material  $x$  in product  $i$ , and  $G_i$  is the global production of product  $i$  in mass units.

$$D_{CRTi} = \frac{D_{Pbi} \times M_{PbO}}{\varepsilon_{Pbi} \times M_{Pb} \times w_f} \quad \text{Eq 2}$$

Where  $D_{Pbi}$  is the global yearly demand for lead metal from product,  $\varepsilon_{Pbi}$  is the efficiency of option  $i$  to extract lead from CRT leaded glass,

$M_{PbO}$  is the molecular weight of PbO,  $M_{Pb}$  is the molecular weight of Pb and  $w_f$  is the mass fraction of CRT leaded glass in CRT glass.

The number of CRT screens needed to supply the demand of CRT leaded glass for each product  $N_i$  was calculated with Equation 3.

$$N_i = \frac{D_{CRTi}}{w_g \times m_{scr}} \quad \text{Eq 3}$$

Where  $w_g$  is the mass fraction of total CRT glass in a CRT screen and  $m_{scr}$  is the mass of a CRT screen.

Information about the materials to be replaced by CRT leaded glass in other products, as well as the mass fraction of the replacement  $w_{CRTxi}$  was obtained from publicly available scientific studies and industry reports [3], [6], [8], [10]–[21]. The global production  $G_i$  of the products in which CRT would replace raw materials was obtained from the International Lead Association [22], Glass Alliance Europe [23], the Ceramic World Review [24] and the US geological survey [25]. The extraction efficiency of lead from CRT leaded glass  $\varepsilon_{Pbi}$  was obtained from six studies evaluating different extraction technologies [6], [10]–[14]. An average value for the mass fraction of CRT leaded glass in CRT glass  $w_f$  was obtained from previous studies on the composition of CRT glass [2]–[4], [8], [26]. The mass fraction of total CRT glass in a CRT screen  $m_{scr}$  was assumed to be 0.85 kg/kg (85%) [1]–[4]; the mass of a CRT  $w_g$  was assumed to be 20 kg.

2. **Indispensability of lead in new product.** Lead was considered indispensable if it accomplished a function in the selected product. The main material and respective function to be replaced by CRT leaded glass in each product was obtained from the available scientific studies and industry reports [3], [6], [8], [10]–[21].

3. **Potential lead leaching during the use phase of the new product.** Lead leaching values from the selected products during use were obtained from the available scientific studies and industry

reports [3], [6], [8], [10]–[21] as well as from independent studies evaluating lead leaching from products [27], [28].

- 4. Retrievability of lead at the end of life of the new products.** Lead was considered highly retrievable if the lead mass fraction in new products was above the current mass fraction in CRT leaded glass. Medium retrievability was assumed when the mass fraction in new products was equal to the current mass fraction in CRT leaded glass and low retrievability was assumed when the new mass fraction was below the current one.

There is limited information regarding technical specifications and capacity of disposal facilities for CRT leaded glass. In this study, we review the disposal options currently used in Europe and the U.S. We also identified repositories for other types of hazardous waste that could be used for CRT leaded glass. The disposal options were reviewed only qualitatively.



### 3. Results

The chemical composition of CRT leaded glass is summarized in Table 1.

Chemical compound	Mass percentage in CRT leaded glass (mass fraction times 100)				
	Funnel		Neck	Total	
	min	max	avrg	avrg	average
SiO <sub>2</sub>	51	64	57	52	54
Al <sub>2</sub> O <sub>3</sub>	1	5	3	2	2
Na <sub>2</sub> O	5	8	7	3	5
K <sub>2</sub> O	6	10	8	12	10
CaO	1	5	3	2	2
MgO	1	3	2	0	1
BaO	0	3	2	2	2
SrO	0	1	0	0	0
PbO	11	24	18	28	23
ZrO <sub>2</sub>	0	0	0	0	0

**Table 1. Average (avrg) chemical composition of CRT leaded glass.**

Values rounded to 2 significant digits. Data sources [1]–[4], [8].

#### Recycling options

The main material to be replaced by CRT leaded glass in most of the products proposed in the literature reviewed was silica or sand. A total of six scientific publications have analyzed the technical feasibility of raw material replacements by CRT leaded glass in four different construction materials: clay bricks, ceramic glaze, concrete and foam glass [3], [15]–[19]. In addition to the silica, manufacturing of ceramic glazes might profit from minor amounts of metal oxides in the CRT leaded glass such as alumina (Al<sub>2</sub>O<sub>3</sub>); which can act as flux in the glaze melting process [16].

Another six scientific publications proposed pyrometallurgical, hydrometallurgical as well as high temperature synthesis methods to extract lead metal from CRT leaded glass [6], [10]–[14]. The efficiency of the methods to extract lead from CRT leaded glass ranged between 90 and 99% of the lead initial content [6], [10]–[14]. The lead extracted may be used in applications such as lead acid batteries.

Two studies carried out in collaboration with industry evaluated the usage of CRT glass as smelting flux in lead and copper smelters [8], [20] and one author proposed the use of CRT leaded glass for nuclear waste vitrification [21]. The lead contained in the CRT glass may provide shielding against gamma radiation in the vitrification of nuclear waste [21].

We found the chemical composition of tableware crystal glass to be similar to that of CRT leaded glass. However, no information about the possible material replacements was found.

In the cases in which lead is not required by the product, e.g., clay bricks, concrete and foam glass, the mass fraction replacements were limited by lead leaching: leaching values increase with higher mass fraction replacements [15], [17], [18].

Similarly, the use of CRT leaded glass as smelting flux in copper smelters was limited by the increase in lead leaching from the smelting slag [20]. In practice, CRT leaded glass is used as flux in several lead and copper smelters around the world [29]–[32]; this has been evaluated as beneficial economically and in terms of direct environmental impacts [8]. However, there is limited information regarding the amounts of CRT leaded glass that could be used in different smelters as well as about the influence of replacing flux by CRT leaded glass in the lead leaching from slag.

Tableware crystal glass might benefit from both the silica and the PbO in CRT leaded glass, considering that crystal glass contains 55 to 65% silica and 7 to 32% PbO [27]. We were however not able to find any study analyzing the usage of CRT leaded glass in crystal glass. Nevertheless, some studies have analyzed lead leaching from crystal tableware. In 1998 and 2000 Guadagnino and colleagues analyzed lead leaching from crystal ware containing different types of beverages [27], [28]. The leaching values were found to be acceptable, because they were 30 to 40% the PTWI level of 25 µg Pb/kg body weight as defined in 1993 by JECFA [28]. However, in 2011, the JECFA withdraw this PTWI after new scientific evidence related the intake values to adverse

cognitive and health effects; the JECFA also concluded that it was “not possible to establish a new PTWI that would be considered health protective” [5].

### Disposal options

Regarding disposal options, the current legislation in Europe categorizes CRT leaded glass under waste containing heavy metals and mandates to dispose it of in landfills for stabilized residues [33].

Backfilling is a waste treatment option considered in the European waste treatment regulation [34]. The term backfilling is defined by the European Commission as “a recovery operation where suitable waste is used for reclamation purposes in excavated areas” [35]. The type of waste used for backfilling must be suitable, meaning “appropriate for the purpose and without causing environmental harm”. Under this definition, CRT leaded glass may be used for backfilling old mines; provided that the materials are later reclaimed. However, we were not able to find information regarding this practice.

The interim storage of CRT leaded glass in a designated storage cell within a landfill has been proposed by the company Kuusakoski Recycling and Peoria Disposal in the United States [36]. According to the company, the CRT leaded glass could be retrieved if “markets support the use of the material or recovery of lead in the future” [36]. The retrievable storage cell “provides safe, cost-effective management of treated CRT glass that meets and exceeds regulatory requirements” [36].

The results of the review are summarized in Table 2.

Recycling Options	Global yearly CRT leaded glass demand	Number of CRT screens needed to supply demand	Indispensability of Pb	Lead leaching	Retrievability	Data sources
	Mega tons (Mt)	Million	yes/no	mg Pb per littler leaching agent	High /Medium/Low	
Lead metal extraction	49*	8 200	yes	n.i	H	[6], [13], [14], [25], [37], [38]
Smelting flux	1**	7	yes	0.01	n.i.	[20], [25]
Concrete aggregate	1 200	200 000	no	1	L	[17], [25], [39]
Clay brick aggregate	26	5 000	no	1	L	[15], [40]
Foam glass manufacturing	n.i.	n.i.	no	0.1	L	[19], [25], [37], [41]
Ceramic glaze manufacturing	0.03	5	no	n.i.	L	[16], [24], [25]
Crystal glass	0.01	1	yes	1	M	[23], [25], [27], [28]
Nuclear waste vitrification	n.i.	n.i.	yes	n.i.	M	[25], [42]

**Table 2. Review of available recycling options for CRT leaded glass.**

Values are rounded to 2 significant digits.

n.i.: no information.

\* based on the demand from lead acid batteries.

\*\* based only on the demand from Cu smelting.

### 4. Discussion

The use of CRT leaded glass as concrete aggregate would represent the largest demand for such glass among the options considered, followed by lead metal extraction and the use as aggregate in clay brick manufacturing. However, lead is not indispensable for neither concrete nor clay bricks. In the case of concrete, CRT leaded glass would replace 10% of the volume of fine aggregates, which in turn represent 30% of the volume in concrete [17]. In the case of clay bricks, CRT leaded glass would replace only 3% of the mass of sand, which represents 55% of the mass in clay bricks [15]. Thus, the large demand for CRT glass in these two products is mainly due to the large masses of product worldwide. According to definition of recycling by the European Waste Framework Directive, and taking into account that lead does not accomplish a function in concrete or clay, the potential low mass fraction replacements (however leading to a large mass replacement due to the large quantities of the construction materials produced worldwide) represent a “dilution” of CRT leaded glass into vast amounts of other materials rather than a recycling of it. Nevertheless, provided that the leaching of lead from these products is kept under regulated limits, these options may be considered as interim storage of CRT leaded glass instead. The lead would be entrapped in the concrete and clay matrixes until the end of life of construction structures, from which the final, environmentally sound, disposal of lead must be guaranteed.

The demand for CRT leaded glass for lead extraction is mainly driven by the global production of lead acid batteries, which is the main application of lead metal nowadays [22], [25]. Even though the efficiency of lead extraction from CRT leaded glass is encouraging (up to 99%), the usage of CRT lead for batteries may be limited by several factors: i) the already high recycling rate of lead from lead acid batteries [43] diminishes the demand for lead from other sources, ii) the supply of primary lead is granted by the fact that primary lead is the main source for metals such as bismuth, thallium and antimony, as well as an important source for silver; the use of CRT lead may be challenged by this supply of primary lead and iii) the

operationalization of lab-scale methods for lead extraction from CRT leaded glass at industrial scale may be challenged by high costs and irregular supply of the raw material CRT glass [44].

The usage of CRT leaded glass as smelting flux in lead and copper smelters has been positively evaluated by Huisman, 2004 in close collaboration with an integrated Cu-Pb smelter in Belgium [8]. There is however limited information regarding the actual extraction of lead from the CRT leaded glass during smelting with primary ores; in other words, regarding the contribution of lead from CRTs to the total lead produced by the smelter. To guarantee the feasibility of this option in different countries with different permitted lead leaching levels from smelting slag it is necessary to have more information regarding the leaching behavior of the slag when using CRT leaded glass as flux. This may be achieved by industrial experiments.

Vitrification of nuclear waste would profit from the lead content in CRT leaded glass: other nuclear waste will be safely captured in the glass matrix and lead would provide shielding against radiation [21]. However, the issue of encapsulation versus inertization of the waste in the vitreous matrixes must be clarified. Some chemical elements, for example most inorganic oxides, act as replacement for silicon into silicate glasses; these elements enter the glass network and are thus *inerted* inside the glass. Other elements, notably monovalent and divalent cations such as sodium and calcium, do not enter the glass network, but integrate in the macro structure of the glass instead; such elements are said to be *encapsulated* in the glass [45], [46]. Lead might “compete” for the glass structure spaces with the other elements in the waste that is being vitrified. Further analyses of the performance of CRT leaded glass for vitrification of different types of nuclear waste are necessary.

Despite the similarities in chemical composition between tableware crystal glass and CRT leaded glass, there is, to our knowledge, no literature

referring to possible raw material replacements by CRT leaded glass. However, even if the technical feasibility of such replacement were proven, the expanding awareness on lead toxicity and likely forthcoming restrictions on lead usage in tableware might invalidate this option.

The interim storage of CRT leaded glass in a retrievable storage cell may ensure the successful entrapment of lead until economically sound quantities of lead or leaded glass are demanded by future applications [36]. For example, the boost of wind and solar energy production may require new stationary lead acid batteries. An assessment of the dynamics of the lead market is however necessary.

Currently, some companies such as NuLife in the United Kingdom are receiving CRT leaded glass for lead extraction in a pyrometallurgical process. Others, such as Camacho Recycling in Spain are producing glaze for floor tiles. Kuusakoski Recycling and Peoria Disposal are applying the retrievable cell storage concept in some states in the United States. About these companies, the Basel Action Network (BAN), under the e-Stewards® recycling Standard, has announced that: i) companies like NuLife have “no operational permitted process for recycling CRT leaded glass”; raising concerns about “potential bankruptcy and abandonment in the future”, ii) Camacho Recycling “creates tiles that are said to be illegal to import into the US due to their heavy metal content”, and iii) the retrievable storage cell from Kuusakoski Recycling and Peoria Disposal should be considered as a disposal option and not as a recycling option under the e-Stewards® recycling Standard [47]. A follow up on these claims is however necessary in order to foster potentially feasible recycling alternatives that are already in place.

The results of this critical review point out that the more compelling recycling options are the usage of CRT leaded glass as smelting flux and as source for lead metal extraction; provided that lead leaching from slag is kept under regulated limits and that the demand for secondary lead is granted.

Products in which lead does not accomplish a function should not be considered as recycling options but as interim storage; such as concrete, clay bricks and foam glass.

Options such as nuclear waste vitrification require additional analysis regarding the indispensability of lead and the ultimate benefits related to radiation shielding.

Disposal options represent an environmentally sound treatment for CRT leaded glass. However, in cases in which the glass is mixed with other hazardous wastes, these options diminish the future availability of lead.

In general, it is still necessary to carry out assessments of the industrial upscaling and economic feasibility of the options in which lead accomplishes a function. Additionally, to assure a stable throughput of CRT leaded glass for the specific products, a country or regional based assessment of the current stock and expected end of life flows of CRT screens is necessary.

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## About the Step Initiative:

“Step envisions to be agents and stewards of change, uniquely leading global thinking, knowledge, awareness and innovation in the management and development of environmentally, economically and ethically-sound e-waste resource recovery, re-use and prevention.”

Step is an international initiative comprised of manufacturers, recyclers, academics, governments and other organizations committed to solving the world’s waste electrical and electronic-e-waste-problem. By providing a forum for discussion among stakeholders, Step is actively sharing information, seeking answers and implementing solutions.

### Our prime objectives are:

- Research and Piloting
  - By conducting and sharing scientific research, Step is helping to shape effective policy-making
- Strategy and goal setting
  - A key strategic goal is to empower proactivity in the marketplace through expanded membership and to secure a robust funding base to support activity
- Training and Development
  - Step’s global overview of e-waste issues makes it the obvious provider of training on e-waste issues
- Communication and branding
  - One of Step’s priorities is to ensure that members, prospective members and legislators are all made aware of the nature and scale of the problem, its development opportunities and how Step is contributing to solving the e-waste problem.

The Step initiative came about when several UN organizations, who were increasingly aware of the growing global e-waste problem, saw the need for a neutral, international body to seek real, practical answers that would be supported by manufacturers, recyclers and legislators alike.

### Step’s core principles:

1. Step views the e-waste issue holistically, focusing on its social, environmental and economic impact – locally, regionally, globally.
2. Step follows the lifecycle of equipment and its component materials from sourcing natural resources, through distribution and usage, to disposal.
3. Step’s research and pilot projects are “steps to e-waste solutions”.
4. Step vigorously condemns the illegal activities that exacerbate e-waste issues, such as the illegal shipments, recycling practices and disposal methods that are hazardous to people and the environment.
5. Step encourages and supports best-practice reuse and recycling worldwide.

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