Background Paper for Evaluating the Use of Cathode Ray Tube (CRT) Glass as a Substitute for Lead Oxide in Ceramic Tile Manufacturing

January 20, 2016

Introduction

On September 10, 2014, EPA issued a letter regarding the use of CRT funnel glass as a substitute for lead oxide in the production of ceramic tiles.[1] CRT funnel glass may be excluded from the Resource Conservation and Recovery Act (RCRA) hazardous waste regulations under the "use/reuse" exclusion (40 CFR 261.2(e)) for hazardous secondary materials used as an ingredient to make a product or used as an effective substitute for a commercial product, as long as that use is legitimate. This paper provides background information that EPA considered in developing that letter.

Note that EPA has no specific testing requirements for products made from recyclable hazardous materials. In order to be legitimate recycling, one of the factors that must be met is that products from the recycling process must be comparable to legitimate products (see 40 CFR 260.43(a)(4)). However, a generator can use any number of methods for making this determination, including using generator knowledge or widely-recognized specifications that address the hazardous constituents, to determine that the product of recycling is comparable to a legitimate product. It is the generator's responsibility to make the determination of legitimate recycling if claiming a recycling exclusion from the regulations, and no prior approval from EPA is required.

In addition, under Section 3006 of the Resource Conservation and Recovery Act (RCRA) individual states can be authorized to administer and enforce their own hazardous waste programs in lieu of the federal program. Under Section 3009 of RCRA, states retain authority to promulgate regulatory requirements that are more stringent than the federal regulatory requirements. Generators should consult with their authorized state agency when making a legitimate recycling determination.

Finally, it should be noted that the use/reuse exclusion would only apply to the processed CRT glass that is legitimately used as an ingredient to make a product or as an effective substitute for a commercial product. CRTs themselves (whether intact or broken) would continue to be regulated under the CRT rule (found at 40 CFR 261.4(a)(22)) or as hazardous waste.

Legitimacy Factor 1: Does the CRT funnel glass provide a useful contribution?

EPA Finding: CRT funnel glass can provide a useful contribution both to the recycling process (firing of ceramics) as well as to the product of the recycling (ceramic tile and glaze).

[1] U.S. EPA (2014). Memo from Barnes Johnson, Director, Office of Resource Conservation and Recovery to Chris York, Sims Recycling Solution, September 10, 2014, RCRA Online 14845.

The use of lead in ceramics has an extensive history and lead is a valuable component of many glasses and glazes. Lead compounds, such as lead oxide (PbO), have historically been used in glaze formulations to regulate the melting properties of other glaze components and to enable the use of a broad firing temperature range in the production process.

In this case, the lead oxide in the CRT glass acts as a flux in the manufacturing process and reduces the energy needed for firing by approximately 10–15%. Additionally, the CRT glass substitutes for up to 15–20% of raw materials (e.g., silica, strontium, clay, feldspar, and barium) in the tiles and glaze.

Benefits of Using Lead Oxide in Ceramic Glaze

Some of the general characteristics of glazes made with lead oxide include:[2]

- *Low Melting Range*. The strong fluxing action of PbO allows the formulation of glazes, which mature at relatively low temperatures in comparison with their leadless counterparts.

- *Wide Firing Range*. PbO in the glaze reduces viscosity and allows for satisfactory maturation over a wider firing range.

- *Low Surface Tension*. PbO imparts low surface tension, which is chiefly responsible for the smooth flow and generally high gloss of these glazes. Low surface tension is the property that contributes to the ability of lead glazes to heal over blisters, drying cracks, and other defects in the glaze surface. Low interfacial tension contributes to the good wetting and adherence of the glaze to the body. Low surface tension coupled with the wide softening range of lead glazes accounts for their superior maturing qualities.

- *High Index Of Refraction*. Brilliant glaze surfaces are attained due to high index of refraction imparted by PbO.

- *Resistance to Devitrification*. The presence of PbO in the glaze reduces any tendencies towards surface crystallization or devitrification of the glaze. Devitrification is the process whereby the surface of the glass develops a whitish scum, crazing (network of fine cracks), or wrinkles instead of a smooth glossy shine, as the molecules in the glass change their structure into that of crystalline solids

Comparison to Lead-less Glazes

Development of lead-less glazes began after World War II in response to shortages of lead oxide. More recent emphasis on leadless glass and glaze development occurred in the 1980's and 90's as environmental, occupational safety, and lead migration regulations became stricter. Three substitutes for the use of lead have been pursued. Direct substitution of bismuth for lead produces adequate

[2] "Lead Glazes for Ceramic Foodware." Dr. Richard Lehman, Rutgers University and The International Lead Management Center.

results. However, bismuth can impart a yellowish color under certain circumstances, the supply of bismuth is limited, the price is high, and the toxicity of bismuth itself may be an issue. A second group of leadless compositions uses zinc and strontium to provide the necessary fluxing. These glazes are glossy and fire well, but color development is poor. A third approach uses alkali borosilicate [ABS] formulations. The ABS glazes are becoming widely used, particularly on bone china due to the high expansion of the ware, but significant problems remain with its use. Higher firing temperatures are required to produce a smooth glaze surface, the leadless glazes react less aggressively at the body interface, defect rates are higher, and decoration is difficult.[3]

Use of Lead Oxide in Ceramics Worldwide

Non-lead glazed ceramic ware is quite common in the U.S. due to the stricter FDA guidelines issued in 1992 for leachable lead from ceramic ware. It is not clear how common lead oxide is used in other countries. It is likely that lead oxide use in Europe is becoming less common due to increasing environmental restrictions imposed by the European Union (EU). The U.S. imports a significant amount of ceramic ware from China and the lead glazed ware from China is subject to an MOU between the two countries.

CRT Glass Recycled into Ceramic Tiles

The use of CRT glass in the manufacturing of tiles is the result of a number of European Union initiatives designed to address the environmental problems associated with waste electrical and electronic equipment (WEEE). This type of recycling was selected by the European Commission as a pilot project under its LIFE + Programme for its potential environmental benefits and contribution to sustainable development.

Legitimacy Factor 2: Are the ceramic tiles a valuable product?

EPA Finding: Ceramic tiles manufactured from processed CRT glass and sold to third parties for use in walls and flooring would be considered a valuable product.

The ceramic tiles comply with the European standard (UNE-EN 14411:2007) for ceramic tiles. Additionally, the ceramic tiles have been independently tested and their integrity verified by the University of Castellon.

The CRT glass recycler, in this case, a foreign entity, has developed four recipes for using CRT funnel glass in ceramic tiles and provides the recipes, along with the prepared glass cullet it sells, to a number of ceramic tile manufacturers in countries such as Belgium, Germany, Great Britain, Greece, Holland, Italy, and Portugal.

[3] Lead Glazes, Dr. Lehman.

The CRT glass recycler says they have 30-35 customers that currently purchase the prepared glass cullet at a rate of 9,000 tons per year. The ceramic tiles are then sold to markets around the world and are used in walls and flooring for residential, commercial, and industrial areas.

Legitimacy Factor 3: Is the CRT glass managed as a valuable commodity?

EPA Finding: The CRT glass appears to be managed as a valuable commodity and managed to minimize loss to the environment.

The CRT glass will be shipped in large Gaylord boxes that are shrink wrapped, which will minimize loss to the environment. Both entities are certified to the International Standard Organization (ISO) standards and the domestic electronics recycler meets third-party recycling standards.

Legitimacy Factor 4: Do the ceramic tiles contain "toxics along for the ride"?

EPA Finding: Information provided by the recycler indicate that the concentrations of lead and cadmium in the ceramic tiles are at levels that meet widely-recognized commodity standards and specifications that address these constituents (i.e., permissible levels set by the European Union (EU) for ceramics intended to come into contact with food).

When glazes are properly formulated and fired at a high temperature, the lead is sealed or "vitrified." However, if the glazes are not properly prepared and fired, lead may leach (i.e. move from the glaze) into food stored in or on the ceramic ware. The problem of lead migration was recognized early in the twentieth century and an increasing level of research was focused on fritting of lead oxides to reduce the lead availability and on understanding the proper formulation of lead glazes to minimize migration by interdiffusion. This effort culminated in the 1974 Geneva Conference on Ceramic Foodware Safety at which state of the art technology was presented. The Conference also laid the groundwork for broad international standards on the test methods and permissible limits of lead and cadmium release from foodware surfaces.

Both the American Society for Testing and Materials (ASTM) and ISO standards prescribe a test method for lead and cadmium extracted from glazed ceramic surfaces (ASTM C738 – 94; ISO Standard 6486). These tests evaluate lead and cadmium released from the surface of glazed tiles over a 24 hour exposure to a 4% acetic acid solution. The procedure of extraction may be expected to accelerate the release of lead from the glaze and to serve, therefore, as a severe test that is unlikely to be matched under the actual conditions of usage of such ceramic ware.

The CRT glass recycler states ceramic tiles made from their product contain "less than 0.001% lead" and "do not leach." The lead is in the form of lead oxide and is vitrified with the rest of the final product. The recycling process requires a firing temperature lower than 1,400°C and thus the lead will not split from the oxygen.

The CRT glass recycler has submitted testing from UNE-EN ISO 10545-15 "Determination of the emission of lead and cadmium in ceramic tiles." The CRT glass recycler says the levels of lead and cadmium could not be detected and reported their results as <0.004 mg/dm^2 for lead and <0.002 mg/dm^2 for cadmium. (See attachment.)

Regulation of Ceramic Tiles in the European Union

Lead and cadmium in ceramic materials intended to come into contact with food are regulated by the EU (Council Directive 84/500/EEC15, October 15, 1984). This Directive sets migration limits for the metals, which might be released from decoration or glazing. In addition, it prescribes an analytical method for the determination of the migration of these two elements. The EU statutory limits for Category 1 (non-fillable) ceramics are 0.8 mg/dm^2 for lead and 0.07 mg/dm^2 for cadmium.

Based on guidance from the European Food Safety Committee, the EU Commission has proposed to reduce the permissible limits for the transfer of lead and cadmium from ceramic materials intended to come into contact with food. Should the EU finalize changes to their limits, the ceramic tiles would need to comply with the new limits.

The Table below compares the current EU statutory limits, the proposed EU statutory limits, and the CRT glass recycler's test results.

Category 1 Ceramics (not fillable ceramics)	**Current EU statutory limits for ceramic material intended to come into contact with food**	**Proposed EU statutory limits for ceramic material intended to come into contact with food**	**Test Results from CRT Glass Recycler**
Lead	0.8 mg/dm^2	0.002 mg/dm^2	<0.004 mg/dm^2 (Could not be detected)
Cadmium	0.07mg/dm^2	0.001 mg/dm^2	<0.002 mg/dm^2 (Could not be detected)

Regulation of Ceramic Tiles in the United States

Unlike the European Union (EU), the United States does not set regulatory levels for lead that would apply to ceramic tiles. [4] The FDA does regulate the sale of tableware (plates, cups, pitchers) that contain lead and tableware exceeding the FDA action levels cannot be sold legally in the U.S.[5] The U.S. Food and Drug Administration (FDA) states the problem is not that ceramics contain lead, but they contain lead in a form that may leach into food.[6]

[4] The United States Consumer Product Safety Commission has banned lead in paint (1977) and toys (2008), but these bans do not apply to glazes or ceramics.
[5] FDA CPG 545-450 "Pottery (Ceramics); Import and Domestic - Lead Contamination," last updated November 2015.
[6] FDA Consumer Update: "Some 'Lead-free' Pottery Can Still Taint Food," November 2010.

According to the FDA, proper firing of ceramics would typically vitrify lead in the glaze and limit any potential for it to leach into food should the ceramic tiles have contact with food. FDA's standard is based on reasonable expectation of migration under intended use conditions, in contrast to the EU ISO standard leach test, which is considered an extreme "stress test" condition.

The FDA action levels for lead in ceramic ware are as follows:

Category	**Guidelines µg/mL (FDA 2000)**
Flatware	3.0
Small Hollowware other than cups and mugs	2.0
Cups/mugs	0.5
Large Hollowware other than pitchers	1.0
Pitchers	0.5

However, the results of the CRT glass recycler's test on the tiles cannot be directly compared to the FDA action levels for ceramic ware to because the test is reported in mg/dm^2 (mass/area) and the FDA action levels are in micrograms/mL (mass/volume). If the intended use of an article would be reasonably expected to result in its migration into food, the manufacturer would have to submit pre-market notification to the FDA for assessment.

Export Regulations

Additionally, because CRT funnel glass managed under the "use/reuse exclusion" would not be RCRA hazardous waste in the United States, the CRT glass would not be subject to notice and consent under U.S. export regulations in 40 CFR part 262 subparts E or H. However, because CRT glass is a listed hazardous waste under the Organization for Economic Cooperation and Development's (OECD)[7] Council Decision it would be subject to applicable regulations in the countries of transit and import implementing the OECD Council Decision. Under Section II.B.4 of the OECD Council Decision, if the waste being shipped is controlled as hazardous by only one of the countries of export and import, then the notice and consent procedures and other associated procedures are administered by the country that controls the waste as hazardous. This is referenced in 40 CFR 262.82(a)(2)(iii).

[7] OECD Council Decision C (2001)107/FINAL on the Control of Transboundary Movements of Waste Destined for Recovery Operations (CRT glass is listed as A2010, "Glass waste from cathode-ray tubes and other activated glasses").

Attachment: Laboratory Test Results on Ceramic Tiles Manufactured Using CRT Glass

(In Spanish Followed by English Translation)

CSIC

LABORATORIO DE ANÁLISIS QUÍMICO

ANÁLISIS QUÍMICO

FECHA:	05-06-2013
N° DE MUESTRAS:	3
DENOMINACIÓN:	Baldosas cerámicas A, B. C
TÉCNICAS EMPLEADAS:	Espectrometría ICP-OES
PERSONA CONTACTO:	F. Rubio

Los análisis de las baldosas denominadas A, B y C, se han realizado siguiendo la norma UNE-EN ISO 10545-15 " *Determinación de la emisión de Plomo y Cadmio en las baldosas cerámicas".*

El ensayo se ha llevado a cabo simultáneamente en seis probetas de cada una de las baldosas (A, B y C)

Se han preparado seis probetas de 7x7 cm^2, de cada una de las muestras. En cada una de ellas se ha aplicado un cordón de silicona (libre de Pb y Cd), alrededor de todo el perímetro de la superficie esmaltada.
En cada una de las probetas se ha adicionado 35ml de ácido acético al 4% y se ha mantenido tapado durante 24 horas.

La determinación del contenido de plomo y cadmio en las soluciones de extracción se ha realizado mediante la técnica de espectrometría de plasma ICP-OES.

Los resultados corresponden a la media de los 6 ensayos:

MUESTRA	Pb (mg/dm^2)	Cd (mg/dm^2)
A	<0.004	<0.002
B	<0.004	<0.002
C	<0.004	<0.002

Chemical Analysis

Date: June 5, 2014
Number of Sample: 3
Title: Baldosas cerámicas A, B. C
Ceramic Tiles A, B, C: Spectrometry ICP-OES
Contact Person: F. Rubio

Analyses of tiles called A, B and C, were performed following the standard UNE-EN ISO 10545-15 "Determination of the emission of lead and cadmium in ceramic tiles."

The test was carried out simultaneously in six samples of each of the tiles (A, B and C).

Six test pieces were prepared 7x7 cm2, of each of the samples. In each of which is assigned a bead of silicone (free of Pb and Cd), around the entire perimeter of the glazed surface. In each of the test specimens was added 35 ml of 4% acetic acid and has been covered for 24 hours.

Determination of lead and cadmium in the extraction solutions was performed using the technique of plasma spectrometry ICP-OES.

The results are the mean of 6 trials:

Sample	PB (mg/dm2)	Cd (mg/dm2)
A	<0.004	<0.002
B	<0.004	<0.002
C	<0.004	<0.002