# METHODS OF RECOVERY OF CRT GLASS WASTE FROM WEEE

# Alin-Marius NICULA<sup>1</sup>, Gabriela-Emilia POPIŢA<sup>1</sup>, Cristina ROȘU<sup>1\*</sup>

<sup>1</sup> Babeş Bolyai University, Faculty of Environmental Sciences and Engineering, 30 Fântânele Street, RO - 400294, Cluj-Napoca, Romania \* Corresponding author: cristina.rosu@ubbcluj.ro

**ABSTRACT.** This paper represents an ample study on hazardous waste came from WEEE, namely CRT glass. The aim of this study was to obtain a composite structural material which would integrate CRT (cone) glass. The hereby study is structured and presented into three main parts: literature data, the experimental part and results interpretation and general conclusions. Chemical analyzes were made with Atomic Absorption Spectrometry method and the lead (Pb) leachability of the new material made was monitored. Also mechanical strength test were made using a Tehnotest device. Mechanical tests were conducted for resistance to compression and flexure of the material. For the new material were obtained good results and it can be viable both from metal leachability and mechanical resistance point of view. The obtained data and results show the possibility to incorporate hazardous waste into new composite materials and represent a foundation for further research and new directions to follow are opened for profound investigation in this area.

Key words: CRT, WEEE, composite material, lead

### INTRODUCTION

Waste began to be increasingly visible in our lives and we can say that their management is one of the challenges of this century. From the many categories of waste some waste of them impresses with by quantity and others via their environmental damage (Gaidajs et al., 2010, Deepak and Pooja, 2013). We chose to focus on hazardous waste from WEEE, specifically those from CRT (Cathode Ray Tube) glass (obtained from IT equipment and TV) which is a hazardous waste (Mueller et. al., 2012). The danger of this waste comes from the frit that have a high level of lead content and the migration possibility of migration into the soil, sub soil and water can occur, and then through different ways can affect human health and environment (Song et al., 2012).

### About WEEE and CRT

Recently, WEEE waste has become increasingly popular and this topic is presented in many contexts (Schumacher et al., 2014). With the understanding of the problems that WEEE uncontrolled landfilling may be caused, the authorities have tightened law in this area. Even that, the problems of WEEE collecting and neutralizing are many and complex (Tung-Chai and Chi-Sun, 2012).

To fully understand the complexity of materials originated from WEEE were presented the major components from WEEE, in Fig. 1.



Fig. 1. Material components of WEEE (Source: Dulamă, 2014)

From the data presented in Fig. 1, it can be seen the multiplicity and diversity of the materials derived from WEEE. Many of them are recyclable in a high percentage. Some of the materials were found in small quantities but significant from economical point of view (Innocenzi et al, 2013). A good example is the precious metals (gold, silver, platinum, yttrium, etc.). Other materials do not have economic importance but fortunately it hasn't hazardous impact on the environment, it can be directly transferred in landfills.



Fig. 2. CRT Components (Source: Courtesy of Robin Ingenthron, Massachusetts Department of Environmental Protection; http://www.dep.state.fl.us)

#### METHODS OF RECOVERY OF CRT GLASS WASTE FROM WEEE

The waste investigated in the present study is a hazardous one which at first glance doesn't have economic attractiveness. In this case were taken two challenges: in terms of scientific research (neutralization and reuse) and economic outlook.

From many available materials, this research was mainly focused on CRT glass derived from TV (Fig.2). It could be distinguished four components of televisions with different percent of lead in CRT glass (Bedekovik, 2015). These components are: front, neck, cone and frit. The lead content in front CRT is between 0-3%, in cone CRT is up to 25%, in neck CRT has a percent about 40%, and in frit CRT the percent is about 70% (Popovici et al., 2013).

## **EXPERIMENTAL**

Several studies demonstrated that CRT glass has been successfully introduced i in several types of composites (Tung-Chai and Chi-Sun, 2014). For this study, was chose the use the cement matrix.

This research had as main objective to obtain a composite material incorporating CRT glass (cone type), which is categorized as hazardous waste. The main objective has other sub-objectives namely: 1) to found if the obtained material correspond to current standards for construction materials and 2) analyze the lead leachability from the CRT incorporated in the material (under the maximum allowed concentration in legislation).

### Description of the recipes, tests and analysis

In order to obtain a composite material incorporating the glass cone CRT were made and tested two recipes denoted R1 and R2. According to empirical determinations for both recipes was chose to the further study the recipe R2 which was more suitable for this type of research. Then, from R2 were formed other recipes denoted: R 2.1, R 2.2, R 2.3, R 2.4, R 2.5 and R 2.6. For the composition of these recipes was used: CRT glass cone, cement, zeolite and water. The materials obtained with these recipes have been analyzed in terms of leachability. The main differences between these recipes are given in Table 1.

Recipe	Diameter glass	Diameter zeolite			
R 2.1	Ø 1-3mm	Ø 0-0,6mm			
R 2.2	Ø 1-3mm	Ø 0,6-2mm			
R 2.3	Ø 7-8mm	Ø 0-0,6mm			
R 2.4	Ø 7-8mm	Ø 0,6-2mm			
R 2.5	Ø >8mm	Ø 0-0,6mm			
R 2.6	Ø >8mm	Ø 0,6-2mm			

 Table 1. Granulometry differences between recipes

#### ALIN-MARIUS NICULA, GABRIELA-EMILIA POPIȚA, CRISTINA ROȘU

#### **Recipes for mechanical tests**

For mechanical tests had changed the recipes numbering, because the first is represented by classic mortar recipe and had no correspondent in recipes for chemical tests. The first recipe, recipe witness R 3.1 is a classic recipe for mortar. In our study, samples obtained from this recipe will be a good benchmark. This recipe has just three components namely: sand, cement and water. The following recipes have components: sand, cement, glass CRT fine granulometry (1-3 mm) zeolite. The recipe R 3.4 is transposition the recipe R 2.5, that was used for chemical analysis. R 3.2 and R 3.3 are recipes intermediate between recipe for classic mortar and R 3.4. Materials used in preparing these specimens were largely similar to those used to obtain material for chemical analysis.

### Chemical analysis

Chemical analyses were divided into three categories. In the first category the material samples were subjected to sonication test. For this test, the material samples were immersed in two types of solution: acidic solution (pH = 3) with ultrapure water and nitric acid (HNO<sub>3</sub>) and an alkaline solution (pH = 12) with ultrapure water and sodium hydroxide (NaOH). Then were introduced in an ultrasonic bath for 30 minutes at room temperature. After completing the process, the solution was filtered and then prepared for AAS (Atomic Absorption Spectrometry) analysis.

In the second category the material samples were subjected to undergone maturation. For this test, the material samples were immersed in two types of solution: acidic solution (pH = 3) with ultrapure water and nitric acid ( $HNO_3$ ) and an alkaline solution (pH = 12) with ultrapure water and sodium hydroxide (NaOH). The samples stayed in the laboratory for five days without suffering any external intervention. After this period the material samples were removed from the solution and the solution was filtered and prepared for the AAS analysis.

In the third category the material samples were subjected to undergone maturation for five days, but with daily adjustment of pH. As was described in the second category were used the same solutions and the pH was daily adjusted. After this period the material samples were removed from the solution and the solution was filtered and prepared for the AAS analysis.

#### Mechanical tests

To demonstrate that the composite material belonging to the category of building materials it was necessary to made several mechanical tests. In this respect were made two tests: resistance to flexure and resistance to compression, both with the device Technotest. The flexural load was applied vertically, with an increase of 50 N/s until the material failed. Normally the fracture must be appeared in a period of 30-90 seconds. Attempts were made with standard: SR EN 1015-11:2002 (SR, 2002). The second test is the resistance to compression. Comparison values and methodology for the tests were taken from standard: SR EN 998-1: 2011 plaster mortars (SR, 2011). For the compression test, material was immersed in water for a period of 2, 7 or 28 days.

# **RESULTS AND CONCLUSIONS**

In order to determine the accurately effectiveness of each recipes the data was processed with accuracy for relevant conclusions. First, the behavior of the material in terms of leachability for each method is presented in the Figs. 3, 4 and 5.



Fig. 3. Leachability of lead from samples subjected to sonication

In Fig. 3, it can be observed that the lead leachability passes over the MAC (Maximum Allowed Concentration for inert waste, from waste legislation for the recipes R 2.1 and R 2.2. The MAC was overcome at alkaline pH = 12.



Fig. 4. Leachability of lead from the samples subjected to maturation with daily pH adjustment

### ALIN-MARIUS NICULA, GABRIELA-EMILIA POPIȚA, CRISTINA ROȘU

In fig. 4 is presented the leachability of lead from the samples subjected to maturation with daily pH adjustment. When material was subjected to maturation for 5 days in two types of solution: acidic and basic (daily adjusted to this pH) a leachability over the concentration 0.2 mg / kg was found for the recipes R 2.1 and R 2.2. The other recipes had very small values of the lead concentration, but was established a correlation between pH and leachability.



Fig. 5. Leachability of lead from the material samples subjected to maturation

The fig 5, presents the leachability of lead from the material samples subjected to maturation for 5 days. Were recorded high levels of lead concentration in leachate, especially for the recipes R 2.1 R 2.2, R 2.3 and R 2.4. Excepting the recipe R 2.3 for the other recipes the MAC was exceeded. The higher lead concentration in leachate was restarted for the material immersed in alkaline solution. Recipes R 2.5 and R 2.6 had a low leachability and don't exceed the MAC of 0.2 mg / kg.

## CONCLUSIONS

### Conclusions for chemical analysis

From the three methods presented above and applied to the material, it can be observed that created recipes had a low lead leachability from CRT glass. Were used several methods in order to better simulate critical situations which could be subject to material during use. Analyzing the methods was calculated the average leachability for each method depending on the pH and were obtained the following values:

- maturation 0.8338 mg / kg to pH = 12 and 0.1739 mg / kg to pH = 3,
- sonication 0.2095 mg / kg to pH = 12 and 0.0051 mg / kg to pH = 3,
- maturation with adjusting the pH daily 0.3331 mg / kg to pH = 12 and 0.0223 mg / kg to pH = 3.

#### METHODS OF RECOVERY OF CRT GLASS WASTE FROM WEEE

It can be seen that sonication method has the smallest average leachability which mean that lead migration is very small in solution. Maturation method without adjustment of pH had the highest leachability of lead. It can be attributed to the alkalifying of the solution because of the cement matrix of the material. It is well known that the cement has alkaline pH.

After analyzing the behavior of the five recipes, the conclusions was that the recipe R 2.5 had all the leachability values under MAC (0.2 mg / kg) (Fig 6). This recipe fits perfectly with the aim of the study Almost all lead concentration values of this recipe are below MAC and shows that the material has a high chemical stability.



Fig. 6. Leachability of lead for the recipe R 2.5

In the Tables 2 and 3 are presented the results for the flexural strength and compressive resistance for the recipe.

Recipe		Force applied for flexural [N]	Flexural strength N/mm <sup>2</sup>		
R 3.1	А	3320	7,78		
	В	3980	9,32		
	С	2410	5,64		
R 3.2	А	2640	6,18		
	В	3440	8,06		
	С	2200	5,15		
R 3.3	А	2220	5,20		
	В	2200	5,15		
	С	2100	4,92		
R 3.4	A	925	2,16		
	В	720	1,68		
	С	1450	3,39		

Table 2. Flexural strength test results

#### ALIN-MARIUS NICULA, GABRIELA-EMILIA POPIȚA, CRISTINA ROȘU

From Table 2 it can be observed that the obtained values for flexural resistance are between 1.68 and 9.32 N/mm<sup>2</sup>. The obtained values were compared with mortar standard which provides that the flexural resistance values range between 0.2 and 2 N/mm<sup>2</sup>. Recipe R 3.1 (classic mortar) has obtained the highest flexural strength and the recipe R 3.4 had the worst results in this regard. Regarding the other two recipes (R 3.2 and R 3.3) it can be observed that the general trend for the flexural strength was to decrease with removing sand and adding CRT glass. The proposed new recipes (R 3.4) have passed this test and are viable for use in production.

Resis- tance	Recipe											
N/mm²)	R 3.1		R 3.2		R 3.3		R 3.4					
	A 2 days	B 7 days	C 28 days									
Rc1	44,2	51,7	44,7	37,7	40,9	47,2	39,9	44,3	44,6	23,3	30,8	43,5
Rc2	50,0	46,4	36,1	38,3	49,2	43,9	40,8	45,2	41,0	23,6	38,3	30,2
Rc average	47,1	49,0	40,4	38,0	45,0	45,5	40,0	44,9	42,8	23,5	34,5	36,9

 Table 3. Compressive resistance test results

From Table 3, it can be observed that the obtained values for the recipes were not satisfactory by comparison with mortars standard SR EN 998-1: 2011 (SR, 2011). The recipe R presented better values for compressive resistance. The decrease of the compressive strength can be attributed to the total elimination of sand and using of CRT glass with big size granulometry. Based on the comparison between standard and the obtained results, the materials belong to class IV CS plaster mortars. Again recipe R 3.4 (selected from chemical analysis R 2.5) had good behavior at test.

The objective of this study was reached, namely to obtain a composite building material that incorporate CRT glass (cone). The obtained material meets the standards present in the environmental legislation (namely waste landfilling) and construction legislation (standards).

### REFERENCE

- Bedekovic G, 2015, The use of air separation in recycling CRT TV sets. *Waste Management,* **38**, pp. 366-371.
- Deepak P., Pooja S., 2013, Chemical modification of waste glass from cathode ray tubes (CRTs) as low cost adsorbent. *Journal of Environmental Chemical Engineering*, **1**, pp. 226-232.
- Dulamă A., 2014, Studies and research on environmental protection by making composite materials encompassing CRT glass waste (PhD thesis, UTCN Cluj-Napoca).
- Gaidajs G., Angelakoglou K., Aktsoglu D., 2010, Environmental Problems and Current Mamangement. *Journal of Engineering Science and Technology Review* **3** (1), pp. 193-199.
- Innocenzi V., De Michelis I., Ferella F., Beolchini Fr., Kopacek B., Vegliò F., 2013, Recovery of yttrium from fluorescent powder of cathode ray tube, CRT:Zn removal by sulphide precipitation. *Waste Management*, **33**, pp. 2364-2371.
- Mueller J., Boehm M., Drummond C., 2012, Direction of CRT waste glass processing: Electronics recycling industry communication. *Waste Management*, **32**, pp.1 560-1565.
- Popovici A., Popița G.E., Roba C., Rusu T., Tofană V., Roșu C., 2013, A proposal for cathode ray tubes waste ray tubes waste recycling. *Journal of Environmental Protection and Ecology (JEPE)*, **14** (4), pp. 1703-1711.
- Schumacher K., Schumacher T., Agbemabiese L., 2014, Quantification and probabilistic modeling of CRT obsolescence for the State of Delaware. *Waste Management*, **34**, pp. 2321-2326.
- Song Q., Wang Z., Li J., Zeng X., 2012, Life cycle assessment of TV sets in China. *Waste Management*, **32**, pp. 1926-1936.
- SR EN 1015-11:2002, Methods of test for masonry mortar
- SR EN 998-1:2011, Specification for mortar for masonry. Part 1, Plastering and plastering mortars.
- Tung-Chai L., Chi-Sun P., 2012, A comparative study on the feasible use of recycled beverage and CRT funnel. *Journal of Cleaner Production*, **29-30** pp. 46-52.
- Tung-Chai L., Chi-Sun P., 2014, Use of recycled CRT funnel glass as fine aggregate in drymixed concrete paving blocks. *Journal of Cleaner Production*, **68**, pp. 209 – 215.
- \*\*\*http://www.dep.state.fl.us/waste/categories/electronics/pages/lead.htm, accessed on November 22.2015.